

OPTIMIZATION OF LOW STYRENE-BUTADIENE RUBBER COMPOUNDS USING RESPONSE SURFACE METHODOLOGY

A Thesis Submitted
in Partial fulfillment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING

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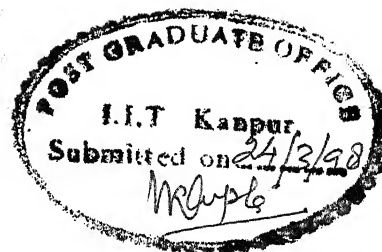
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March , 1998

CERTIFICATE



Dated March , 1998

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OPTIMIZATION OF LOW STYRENE-BUTADIENE RUBBER COMPOUNDS USING RESPONSE SURFACE METHODOLOGY

ABSTRACT

Rubber compounds (elastomers) find wide applications in rocketry and space technology. A few of which include insulation for solid rocket motors, liner materials, liquid propellant storage bladders, o-rings, gas seals, compression gaskets and vibration isolators. To meet the specific requirements of usage, the rubber compound in question must have the desired mechanical and thermal properties. These properties are governed by a wide range of parameters like : the type of base rubber and the type and composition of compounding ingredients (sulfur, accelerator, filler, plasticizer, etc.)

The influence of two most significant parameters viz. curator (sulfur) and accelerator (CBS) levels on the mechanical properties and cure characteristics of Low Styrene-butadiene rubber compounds have been studied. Central composite design was used to limit the number of compounding trials to the minimum and provide maximum information at the same time. Regression models (for properties evaluated) which adequately fit the experimental data were obtained. Contour diagrams and response surfaces were plotted for these model response equations. From this the optimum values of curator (sulfur=2.0 phr) and accelerator (CBS=2.1 phr) in the rubber compound for achieving the desired mechanical and cure properties of Low Styrene-butadiene rubber compound were determined.

The variation in stress-strain characteristics and dynamic behaviour of LSBR compounds with change in vulcanization system (sulfur/accelerator ratio) and change in filler loading have been investigated. The glass transition temperatures, T_g for these compounds have been determined from the dependence of storage modulus and loss tangent on temperature.

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ABBREVIATIONS

ACCINOX TQ : Trade-name for 2,2,4-trimethyl-1,2-dihydroquinoline

CBS : N-cyclohexylbenzothiazole-2-sulfenamide

DCBS : N,N-dicyclohexylbenzothiazole-2-sulfenamide

EGL : Effective gauge length (of a tensile test specimen)

EPR : Ethylene-propylene rubber

GPF : General purpose furnace (carbon black)

LSBR : Low styrene-butadiene rubber

MBTS : Benzothiazyl disulfide

NR : Natural rubber

PPD : Piperidine pentamethylene dithiocarbamate

phr : parts per hundred

RSM : Response surface methodology

SSE : Sum of squares, residual

SS_{LOF} : Sum of squares, due to lack of fit

SS_{PE} : Sum of squares, due to pure error

SSR : Sum of squares, due to model

TMTD : Tetramethylthiuramdisulfide

TSS : Total sum of squares

NOMENCLATURE

b_{ij} : coefficients of regression equation or polynomial fit

E^* : complex modulus

E' : storage modulus

E'' : loss modulus

k : number of factors (predictor variables)

m : replications at the centre point

M_{100} : modulus, tensile stress at 100% elongation

M_{300} : tensile stress at 300% elongation

N : total number of experiments

r : rate of vulcanization

R^2 : coefficient of determination

t_0 : original thickness of the sample (mm)

t_1 : final thickness of the sample (mm)

T_g : glass transition temperature

X_1 : coded level of sulfur

X_2 : coded level of CBS

X_i : predictor variables

Y_i : response variables

Y_u : value of response for u combination of factors

Greek symbols

ω : angular frequency of sinusoidal excitation

$\tan \delta$: loss tangent

ϕ : functional relationship

ϵ : strain

ϵ_u : error

σ : stress (ksc)

GLOSSARY

- Accelerator : The compounding ingredient used to shorten the uneconomically long vulcanization time. It also influences the final properties of the rubber compound.
- Activator : In order to produce their full effect, organic accelerators almost require the presence of organic and/or inorganic activators.
- Age resistor : All those additives which prolong the useful life of a rubber or rubber product.
- Antioxidant : A compounding material when added to rubber to prevent its deterioration caused by oxygen.
- Blocking : Portion of the experimental material that is expected to be more homogeneous than the aggregate.
- Compounding : The process of incorporating ingredients with raw rubber.
- Contour graph/ Contours : A graph, the two axes of which show the varying quantities of the two predictor variables, while the curves link points of equal property value.
- Conventional vulcanization system : A vulcanization system in which sulfur to accelerator ratio is high and mainly polysulfidic links ($-C-S_x-C-$, $X>2$) are formed.
- Crosslinking : Linking of macromolecules at their reactive sites.
- Curator : Compounding ingredient that crosslinks the raw rubber so as to improve the mechanical properties.
- Degree of vulcanization : Number of crosslinks formed per unit weight or volume of rubber compound.
- Die swell : The effect wherein the cross-sectional area of the extrudate (polymer) is usually greater than the cross-sectional area of the extruder die.
- Dynamic mechanical test : It measures the response (deformation) of a polymer to a sinusoidal or other periodic stress.
- Effect : Change in the average response between two factors-level combination or between two experimental conditions.
- Efficient vulcanization system : A vulcanization system in which sulfur to accelerator ratio is low and mono- and di-sulfidic links dominate in the vulcanizate.

Elastomer : A material which can extend in dimension several hundred percent on application of stress, with virtually immediate recovery on release of stress.

Experimental region (factor space) : All possible factor-level combinations for which experimentation is possible.

Factor : Predictor variable

Filler : A compounding ingredient which reinforces the property of rubber and at the same time reduces cost.

Flash : Excess rubber flown out of the mould joints during press vulcanization. This is to be trimmed before use.

Glass transition temperature : The temperature at which a polymeric material transforms itself from a hard rigid glassy state to a somewhat soft and flexible substance at moderate rates of deformation.

Interaction : Existence of joint factor effects in which the effect of each factor depends on the levels of the other factors.

Masterbatch : A homogenous mixture of rubber and one or more materials in known proportions for use as a raw material in the preparation of the final compound.

Mastication : The process by which an elastomer is subjected to intensive working so as to reduce its molecular weight and make it more plastic, capable of flowing and shaping.

Nip : Least distance between the two rollers of a roll mill.

Plasticizer : A compounding material used to enhance the deformability of a polymeric compound.

Predictor variable : A controllable experimental variable that is thought to influence the response.

Processibility : Ease in compounding and shaping of the elastomeric material.

Processing safety : The ability to resist premature vulcanization or scorch during processing and shaping of the rubber compound.

Replication : Repetition of an entire experiment or a portion of an experiment under two or more sets of conditions.

Response : Outcome or result of an experiment.

Response surface : A geometric representation obtained when a response variable is plotted as a function of one or more predictor variables.

Response surface methodology : Collection of techniques for exploring relationships. It includes experimental designs and model fitting and diagnosing techniques.

Rotatable design : When fitting specified response surface models, a design is rotatable if fitted models estimate the response with equal precision at all points in the factor space that are equidistant from the centre of the design.

Rotatability : The property by which the variance of any design point is a function only of the distance of that point from the centre of the design.

Scorch : Prematured vulcanization. It is very undesirable during processing of rubber compounds.

Scorch time : the time at a given temperature (generally two units above the minimum viscosity) at which the crosslinking reactions start and there is an abrupt increase in the torque value.

Semi efficient vulcanization system ; A vulcanization system in which ratio of sulfur to accelerator is between conventional and efficient vulcanization system.

Softener : A compounding ingredient used in small proportions to soften a vulcanizate or facilitate processing or incorporation of filler.

Synergism/Synergistic mixture : The net effect of two accelerators together in a rubber system is much higher than the sum of the effect produced separately by one accelerator.

Tack : The ability of unvulcanized rubber to stick to itself (without necessarily being sticky to other surfaces)

Viscoelasticity : The property by which a material exhibits both, the characteristics of an elastic material which has a capacity to store mechanical energy with no dissipation of energy and a viscous fluid which in a nonhydrostatic stress state has a capacity for dissipating energy, but none for storing it.

Vulcanization : A process by which elastomeric materials or rubbers are converted into a three dimensional network by tying together independent chain molecules.

CHAPTER 1

INTRODUCTION

A unique characteristic of rubbers is their ability to sustain large deformations under applied load and their capability to nearly completely recover the original shape once the load is removed. This rubbery behaviour is shown by many materials, polymeric in nature, of which the first to be used was natural rubber. This natural product is now complemented by a range of synthetic materials which have better characteristics like heat resistance, oil resistance, resistance to burning and low air permeability.

Till 1930, only rubber available was natural rubber. Nevertheless it was able to produce a diversity of products such as tyres, elastic bands, erasers, ebonite battery boxes, rubber floorings, cables and shoe soles by judicious use of additives, giving products with wide ranging properties using a variety of formulations.

With an ever-increasing range of synthetic polymers and additives available now, there is a greater scope for tailoring formulations to meet desired specifications and cost.

At present, the major emphasis of rubber industry to meet the requirements of the automotive industry with about 60% of new rubber being consumed in tyre products alone. Widely used rubbers in tyres (natural rubber, SBR and polybutadiene rubber) comprise about 80% of the world rubber supply in tonnage terms. Other rubbers are the ethylene propylene and chloroprene rubbers, which are widely used in the general rubber goods industries constitute merely 5% of the market.

As the specifications by the automotive industry have become more stringent there has been particular interest in the specialty rubbers. Modern cars utilize chlorosulphonated polythene elastomers in power steering hose, ethylene-propylene rubbers in radiator hose, tail-light gaskets and window seals, ethylene-acrylic rubbers in axle and prop shaft seals and crankshaft dampers, fluoroelastomers for valve stem seals and O-rings, epichlorhydrin rubbers for control system hose, acrylic rubbers for pinion seals, and silicone rubbers for spark plug boots. 'Puncture-proof' rubber fuel tanks are used in racing cars.

The ability to obtain flexible, non-melting, heat-resisting and non-burning materials is of particular value in aerospace, marine and underground applications. Synthetic rubbers are also of particular value in the high-temperature environments encountered in automotive under-the-bonnet insulation applications. The toughness of rubbers makes them particularly suitable for power cable jacketing.

In Civil Engineering, natural rubber and chloroprene rubbers are now widely accepted for bridge bearings while ethylene-propylene and butyl rubbers are important for reservoir lining. Other important uses include conveyor belting, power transmission belting, fire hose liners, vibration insulation pads, dock fenders and chemical plant equipment such as valve diaphragms.

Medical uses of rubbers include blood transfusion and dialysis tubing, hypodermic syringe seals, condoms and baby's dummies. In sports and recreation activities rubbery materials are used for squash and tennis balls and fabric coatings for balloons and inflatable boats.

Familiar uses in the household include shoe-soles and heels, carpet backings and elastic bands.

In rocketry and space applications, a variety of elastomers find use as rocket motor insulation, liner material between the propellant and insulation, gaskets, dust seals, O-rings, vibration isolators and hermetic seals. They are also employed as rubber pads bonded to metal shims in flexible joints of movable nozzles of solid rocket motors. They find application as bladders for storing liquid propellants for the reaction control system of the satellite.

With the requirements becoming stringent, the technical specifications are now much more demanding than in the past. Thus the correct choice of elastomer and the right proportion of its ingredients (compounding agents) play a crucial role in determining the success of any product.

The compounding, mixing, and testing of rubber stock covers a formidable array of materials and techniques. A recurring problem in compounding is to find a formulation which simultaneously meets several constraints. Finding such a formulation can be difficult because improvements in one key property are often gained at the expense of one or more other properties of interest. Response surface methodology comes handy in optimizing these properties by aiding selection of a proper formulation which would meet the desired properties.

CHAPTER 2

LITERATURE REVIEW

2.1 TYPES OF ELASTOMERS

Natural rubber :

Natural rubber is cis-1,4-polyisoprene. Commercially all natural rubber is derived from the tree, *Hevea brasiliensis*. The milky, rubber bearing fluid in the tree is called latex and is obtained by a process called tapping. Natural rubber is obtained by further processing of this latex.

Natural rubber is not oil resistant and is swollen by aromatic, aliphatic, and halogenated hydrocarbons [Bhowmick,1994]. It can be crosslinked by the use of sulfur, sulfur donor systems, peroxides, isocyanate cures, and radiation. Sulfur content of 2-3 phr and accelerator levels of 0.2-1.0 phr are considered to be conventional cure system. Glass transition temperature, T_g is around -72°C [Brysdon,1988].

Natural rubber can strain crystallize, which results in its compounds exhibiting high tensile strength and good tear strength. It can be chemically modified to *epoxidized natural rubber* by introducing epoxide groups at random onto the natural rubber molecule. This leads to increased oil resistance and greater impermeability to gases, as well as an increase in the glass transition temperature, T_g and damping characteristics, while retaining the excellent mechanical properties of natural rubber.

Polybutadiene rubber:

Polybutadiene rubber is produced by solution polymerization. High cis-1,4 polymer content (>90%) rubber would have a T_g around -90°C , and hence exhibits excellent

low temperature flexibility. They also exhibit excellent resilience and abrasion resistance. As the 1,2-vinyl content increases, the low temperature properties, abrasion resistance, and resilience become inferior. The unsaturation present in the main chain necessitates protection against oxygen, u v light and ozone. Oil resistance is poor, and the polymer is not resistant to aromatic, aliphatic and hydrogenated hydrocarbons.

Polybutadiene based compounds can be cured by sulfur, sulfur donor systems, and peroxides. Less sulfur and a higher level of accelerators are required for curing compared to natural rubber [Bhowmick,1994].

Polychloroprene rubber :

Polychloroprene rubber also called as Neoprene rubber is produced by free radical emulsion polymerization [Barlow,1988]. If chloroprene is polymerized without any modifiers, the product is so tough and insoluble that it is impossible to be processed for compounding. The polymer chain has to be broken up to allow points for cleavage.

There are two methods used to obtain processability :

1. The sulfur or thiuram-modified process, and
2. The nonsulfur-modified process

Accordingly the polychloroprene is graded as G-type or W-type. The chlorine atom in the repeat unit has a tendency to deactivate the double bond in the main chain [Bhowmick,1994]. Thus polychloroprene tends to resist oxidation, ozone, and u v light to a higher degree than the other unsaturated rubbers. The chlorine atom also confers an increased level of resistance to oils. Polychloroprene is also self-extinguishing in flame tests. Metal oxides are principally used for curing these materials. The most widely used cure system is based on a combination of the oxides of magnesium and zinc.

Butyl rubber :

Butyl rubber is prepared by copolymerizing small amounts of isoprene with polyisobutylene. The isoprene content of the copolymer is normally quoted as the “mole percent unsaturation”, and it influences the rate of cure with sulfur, as well as the resistance of the copolymer to attack by oxygen, ozone, and u v light.

Chlorobutyl and bromobutyl rubbers are modified types containing 1.2% chlorine or bromine, the isoprene unit being the site of halogenation. Introduction of the halogen gives greater cure flexibility and enhanced cure compatibility in blends with other diene rubbers. It also confers increased adhesion on other rubbers and metals.

Butyl rubber is not oil resistant. Butyl and the halogenated butyl rubbers can be cured by sulfur, dioxime, and resin cure systems. In addition the halogenated types can be crosslinked with zinc oxide and diamines. Peroxides cannot be used because they tend to depolymerize the polyisobutylene.

Nitrile rubber :

Nitrile rubbers are copolymers of butadiene and acrylonitrile produced by emulsion polymerization [Bhowmick,1994]. The introduction of acrylonitrile into the polymer backbone imparts oil resistance and affects many other properties. The acrylonitrile content can vary between 18-50%. The glass transition temperature, T_g for 50:50 copolymer is about -2°C . Higher acrylonitrile content leads to lower resilience, greater hardness and higher compression set, which are undesirable features.

Nitriles have good resistance to oil, aliphatic and aromatic hydrocarbons, and vegetable oils, but they are swollen by polar solvents such as ketones. The unsaturated main chain means that protection against oxygen, ozone and u v light is required.

Nitrile rubbers can be cured by sulfur, sulfur donor systems, and peroxides. Metal oxides can be used to cure the carboxylated nitriles.

Ethylene Propylene Methylene (EPM) and Ethylene Propylene Methylene Diene (EPDM) rubbers :

The ethylene-propylene rubbers are produced by a polymerization process using anionic coordinated catalyst systems developed by Natta and his research team at Milan. The glass transition temperature, T_g , is at its lowest (-50°C) with a propylene content of about 40% [Bhowmick,1994]. One disadvantage of the copolymer is that it cannot be crosslinked with sulfur because there is no unsaturation in the main chain. To overcome this difficulty, a third monomer with unsaturation is made pendant to it. Since the main chain of both EPM and EPDM rubbers is saturated, both co- and ter-polymers exhibit excellent stability to oxygen and u v light and are ozone resistant. EPM and EPDM rubbers are not oil resistant, and they are swollen by aliphatic and aromatic hydrocarbons, as well as by halogenated solvents. They have excellent electrical properties and stability to radiation. Adhesion to metals, fabrics, and other materials can be difficult to accomplish. The copolymers can be cured only by peroxides or radiation, while the ter-polymers can be cured with peroxides, sulfur systems, resin cures, and radiation.

Styrene-Butadiene rubber

Styrene-butadiene rubber can be produced by both emulsion and solution polymerization techniques. Cold polymerization yields polymers with properties superior to those of the hot polymerized types [Brysdon,1988]. One of the most important variables which governs the glass transition temperature, T_g , is the monomer ratio in the copolymer. Polystyrene has a glass transition temperature, T_g , of about

90°C, while polybutadiene has a glass transition temperature, T_g is about -90°C. As the weight fraction of styrene in the copolymer decreases the T_g also decreases which is a desirable characteristic.

Normally available grades of SBR contain about 23.5% bound styrene with a T_g of around -50°C. Another grade of solution SBR, with somewhat low styrene content of 18%, has a T_g of -75°C. SBR is an unsaturated hydrocarbon polymer. Hence unvulcanized compounds will dissolve in most hydrocarbon solvents while cured stocks show extensive swelling. SBR will also prone to reactions such as oxidation, ozone attack, halogenation and hydro-halogenation.

SBR exhibits significantly lower resilience than natural rubber, so that it has higher heat buildup on flexing. It can be cured by the use of sulfur, sulfur donor systems, and peroxides. Sulfur cures generally require less sulfur (1.5-2.0 phr) and more accelerator than normally are required to cure natural rubber.

There are a few other rubbers which suit specific purposes. These are :

Fluorocarbon rubbers: These have the best heat stability. These can give extended service life at temperatures exceeding 250°C.

Silicone rubber : These also exhibit good resistance to heat aging and are considered to be usable upto 200°C. Although silicones do not exhibit high strength at room temperatures they do retain their properties at high temperatures to a much greater extent than other rubbers.

2.2 COMPOUNDING INGREDIENTS

A number of ingredients are added to the raw elastomer to modify its physical and chemical properties. In any one compound, two or more of the following types of compounding ingredients may be used:

- A polymer
- A vulcanizing agent
- A cure accelerator (s)
- A filler
- A softener / process aid / tackifier
- A plasticizer
- A protective agent (s)
- Miscellaneous ingredients : pigments and blowing agents.

The objective in using a particular ingredient is :

1. to improve the physical properties of the rubber;
2. to improve the processing properties of the rubber;
3. to crosslink the rubber compound;
4. to control the rate of cure;
5. to prolong the service life of the rubber;
6. to extend the service range of the rubber; and
7. to reduce the cost of the rubber compound.

2.2.1 Vulcanizing Agents

There are four curing (vulcanizing) agents or systems in widespread use. They are:

1. Sulfur systems;
2. Peroxides;
3. Urethane crosslinkers; and
4. Metallic oxides (used for vulcanizing chloroprene).

By far the most common vulcanizing methods are those dependent on sulfur. The properties of the vulcanizate depend on the number and type of the crosslinks formed. The number of crosslinks formed will depend on the amount of the cure agent added and the cure time. Increased amounts of cure agent will generally increase the number of crosslinks, with the following effects on the final properties of the elastomer:

Modulus, hardness will increase.

Permanent set, elongation at break, and the degree of swell in a solvent will decrease.

Tensile strength and tear strength will generally go through a maximum and then decrease with an increasing degree of crosslinking.

Some cure systems can revert at the cure stage, that is, the number of crosslinks decreases if long cure times or high temperatures are employed at this point and this reversion will cause a reduction in most properties.

Other cure systems exhibit an effect termed "marching modulus" which means that modulus continues to increase with increased cure time.

Sulfur cure

The properties of a sulfur-cured vulcanizate depend on the number and type of crosslinks formed. Figure 2.1 illustrates the types of sulfur crosslink that can be formed during vulcanization by sulfur. The type of crosslink produced depends on the accelerator type and accelerator/sulfur ratio.

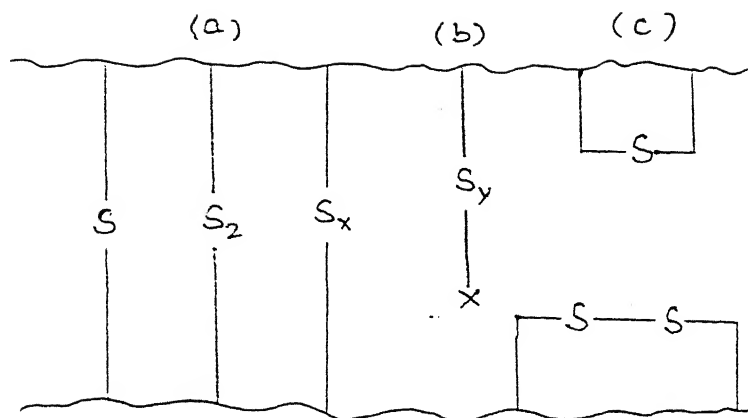


Fig.2.1: Types of Sulfur crosslinks : (a) mono-sulfidic, di-sulfidic and polysulfidic (b) pendant sulfur (c) intramolecular linkages. Types (b) and (c) are wasteful of sulfur

Polysulfidic crosslinks will give better fatigue properties but poorer compression set and aging properties. Monosulfidic crosslinks will give better aging properties and compression set, but poorer fatigue properties. Semi E.V. systems give intermediate properties.

Only unsaturated rubbers, or rubbers with pendant unsaturation, can be vulcanized with sulfur. For natural rubber, with a high level of unsaturation, vulcanization takes place readily, but in polymers where the unsaturation is low (e.g. butyl), vulcanization is slow, hence generally requires more active accelerators.

A conventional vulcanization system (CV) for natural rubber would generally contain 2.0-3.5 phr of sulfur and 0.5-1.0 phr of an accelerator. As the level of accelerator is increased, the amount of sulfur must be reduced if a constant crosslink density is to be

maintained, hence the number of atoms in the sulfur crosslink is reduced. The so called efficient vulcanizing (EV) systems utilize accelerator levels of 3.0 phr plus (with low levels of sulfur), but at least one of the accelerators must be a “sulfur donor”.

2.2.2 Cure activators

Activators are substances which increase the effects of accelerators. Relatively small additions of an activator to a compound considerably increases the degree of vulcanization.

Organic accelerators always require the presence of organic and/or inorganic activators. Zinc oxide is the most important inorganic activator, but magnesium and lead oxide are also used as activators. The fatty acids (e.g. stearic, palmitic, and lauric acids) are the most important organic activators.

The mechanism by which ZnO and stearic acid speed up the cure has not been exhaustively studied and results to date indicate its complexity [Barlow,1988]. It appears that zinc oxide reacts with the stearic acid to form zinc stearate which is soluble in rubber and in this form facilitates the crosslinking process. It is essential to have the zinc ions in soluble form.

2.2.3 Accelerators

The reaction of rubbers with sulfur is slow, even at elevated temperatures. Unaccelerated sulfur cures are lengthy and do not yield a good property spectrum. Therefore the sulfur vulcanization of all unsaturated elastomers is modified by addition of accelerators to speed up the reaction. Commonly used accelerators are given in table 2.1:

Table 2.1: Commonly used accelerators

Class	Typical member and abbreviation	Curing speed
Guanidines	Diphenylguanidines (DPG)	Slow
Aldehyde amines	Complex mixture of aldehyde and amines	Fast
Dithiocarbamates	Zinc dimethyldithiocarbamate (ZMDC)	Very fast
Thiuramsulfides	Tetramethylthiuramsulfide (TMTD)	
Thioureas	Ethylene thiourea (ETU)	Medium
Thiazoles	2-Mercaptobenzothiazole (MBT)	Medium
Sulfenarnides	N-cyclohexyl-2-benzo-thiazolesulfenamide (CBS)	Fast
Xanthates	Zinc dibutyl xanthate (ZBX)	

From the processing viewpoint, the following features of an accelerator are usually desirable [Brysdon,1988].

1. Good processing safety, i.e. longer scorch times to reduce the chance of premature vulcanization during mixing and shaping.
2. Rapid curing at vulcanization temperatures.
3. High cross-linking efficiency.
4. Solubility in the rubber so that there is good dispersion and freedom from blooming.
5. Freedom from reversion effects.
6. Good storage stability.
7. No adverse reactions with other additives.
8. Freedom from health and handling problems.

Different rubbers have different levels of reactivity so that in accelerated sulfur vulcanization what may be a fast-curing system for one rubber may be too slow for practical use in another. Variation in formulations may be needed in order to alter cure

time, scorch time, modulus, aging, fatigue life, reversion resistance, crystallization tendencies and low temperature properties.

Sulfenamide accelerators

The use of sulfenamide accelerators in the sulfur vulcanization of unsaturated rubbers result in a longer scorch but a more rapid rate of cure. The accelerators TBBS, MBS, and DCBS give greater processing safety than the most common sulfenamide accelerator, CBS while TBBS gives the highest state of cure [Bhowmick,1994] as shown in figures 2.2 and 2.3. The thiurams and dithiocarbamates can be used as secondary accelerators to increase the speed of cure, and sulfenamides can be used as secondary accelerators to the former types to increase the scorch time and to decrease the rate of cure.

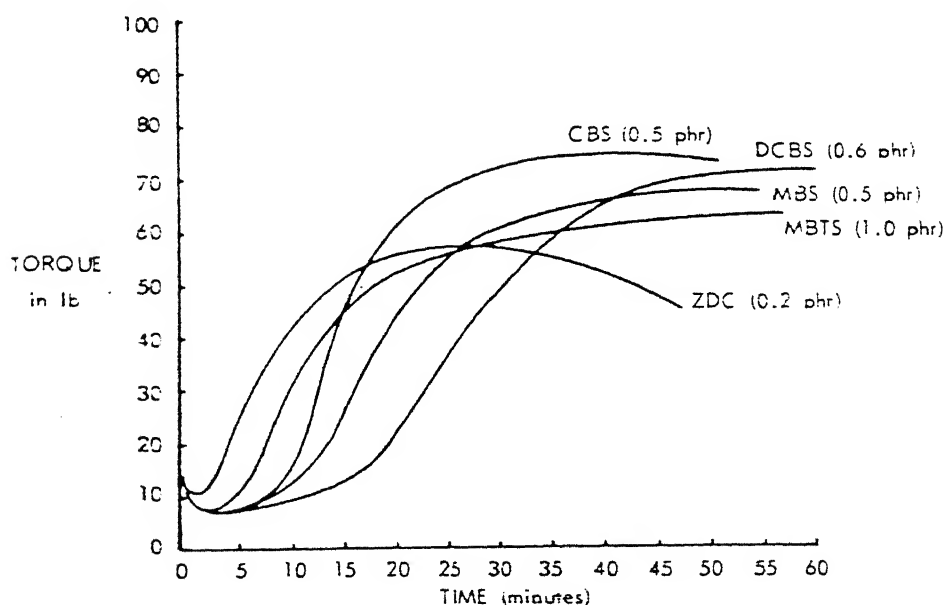


Fig. 2.2: Effect of cure system on cure characteristics. Rheometer at 140°C
Formulation : NR, 100; N330, 50; processing oil, 8; zinc oxide, 5; stearic acid, 2; PPD, 2; sulfur, 2.5 [Brysdon,1988]

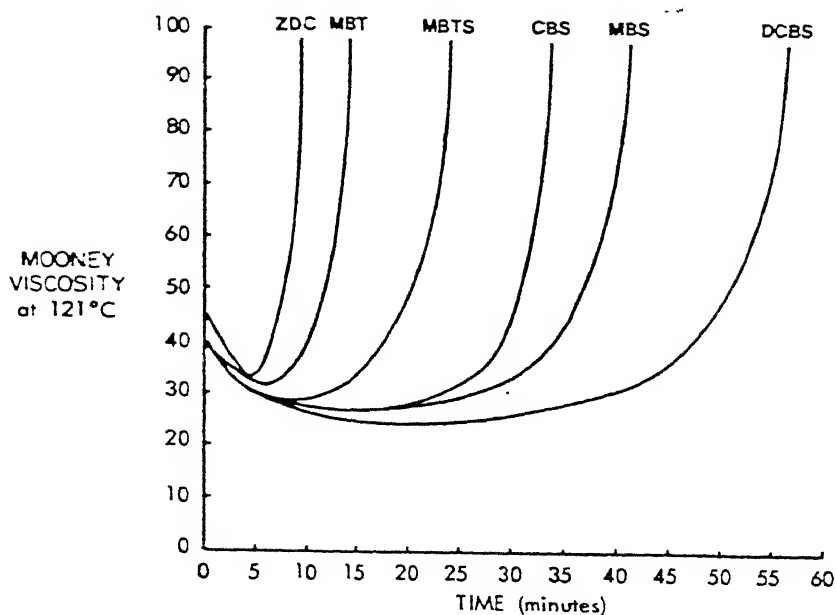


Fig. 2.3: Effect of cure system on scorch time.

Formulation : NR, 100; N330, 50; processing oil, 8; zinc oxide, 5; stearic acid, 2; PPD, 2; sulfur, 2.5 [Brysdon,1988]

Sulfenamides are used in semi-EV and EV cure systems occasionally as the only accelerator. The sulfenamides cannot be used to give sulfurless cure. With the sulfenamides, the following guideline is useful :

Processing safety : $\text{CBS} \leq \text{TBBS} < \text{MBS} < \text{DCBS}$

Modulus : $\text{DCBS} < \text{MBS} < \text{CBS} < \text{TBBS}$

Cure rate index : $\text{DCBS} < \text{MBS} < \text{CBS} < \text{TBBS}$

2.2.4 Filler

Fillers of many types can be added to rubber compounds to extend the range of physical properties, to reduce the cost of the compound, to modify the processing properties (e.g. to achieve a reduction in die swell) , and to influence the chemical resistance of the compound. In addition the fillers can pigment a compound, impart conductivity to it, and influence its aging characteristics.

A reinforcing filler can be defined as a filler that improves modulus, tensile strength, and tear and abrasion resistance. However this improvement in properties is not continuous, when the volume percentage of filler further increases, the point at which there is insufficient rubber to bind the filler together eventually will be reached. A noticeable decrease in strength would happen well before this point.

Commonly used fillers are carbon blacks, silica and silicates, clays, calcium carbonate, barium sulfate and hydrated alumina.

2.2.5 Softeners, Process aids and Tackifying resins

The general purpose of adding these ingredients are :

1. to improve the processing properties;
2. to modify the final compound properties (hardness and flexibility);
3. to alter the cost of the compound; and
4. to reduce power consumption during processing.

Plasticizers also act as softeners and process aids but this item is reserved for an ingredient added for the purpose of lowering the T_g of a polymer.

Commonly used softeners are Petroleum oils.

Process aids are: fatty acids, metal salts of the fatty acids .

Tackifiers are: Resins, pine tar and other hydrocarbon resins which increase the 'tack' of compound in the uncured state.

2.2.6 Plasticizers

Ester plasticizers are used to improve processibility, to improve low temperature properties, and to balance the swelling effects of fuels and oils with which rubber products are frequently in contact [Bhowmick,1994].

The use of ester plasticizers enable larger quantities of filler to be added to the rubber without the compound becoming too stiff to process. Because they also reduce the temperatures generated during processing, which substantially reduces the risk of premature vulcanization (scorch). The addition of ester plasticizers can also reduce compound costs and improve extrusion and calendering characteristics.

2.2.7 Protective agents

Rubber compound is subjected continuously to undesirable changes caused by several agencies. These are oxidation, metal-catalyzed oxidation, u v attack, flex cracking, ozone attack and hydrolytic attack. This can be prevented using protective agents like antioxidants, u v screens, u v inhibitors and hydrolytic stabilizers.

2.3 VULCANIZATION

Vulcanization is the process by which mainly plastic rubber is converted into the elastic rubber or hard rubber state. The process, which is brought about by the linking of macromolecules at their reactive sites, is also known as crosslinking.

2.3.1 Influence of Temperature on the Rate of Vulcanization

Vulcanization like all chemical reactions, naturally gets faster as the temperature rises. Like most chemical reactions it complies approximately with van't Hoffs' law, according to which the velocity of the reaction is approximately doubled or the reaction time is halved, for every 8-10 °C (corresponding to about 1 atm. gauge vapour pressure) by which the temperature is raised.

2.3.2 Modification of Properties by Vulcanization

Vulcanization is a process by which the elastomer-plastic material (raw rubber) is converted into the final elastomer - elastic product. The modulus, hardness, elastic

properties, resistance to swelling, etc. are considerably modified during the progress of vulcanization.

The extent of changes is governed by the choice of the vulcanization process, and also by the vulcanization conditions. Other properties, such as the tensile strength, gas permeability, low temperature flexibility, and electrical resistance change to a lesser extent with the degree of vulcanization.

To obtain rubber products with the best possible properties (which differ greatly according to the application concerned), it is therefore always necessary to use the most suitable combination of vulcanization auxiliaries and the most suitable vulcanization conditions, though, of course, economic considerations have also to be taken into account.

2.3.3 Vulcanization Methods

2.3.3.1 Vulcanization in a Press

While there are different vulcanization methods (like vulcanization in a press, open cure, vulcanization in water and cold vulcanization to suit the requirements), vulcanization in a press has been used in the present investigation due to its simplicity.

2.4 VULCANIZATION STAGES

The vulcanization process can be described by a rheometer curve which can be divided into three stages:

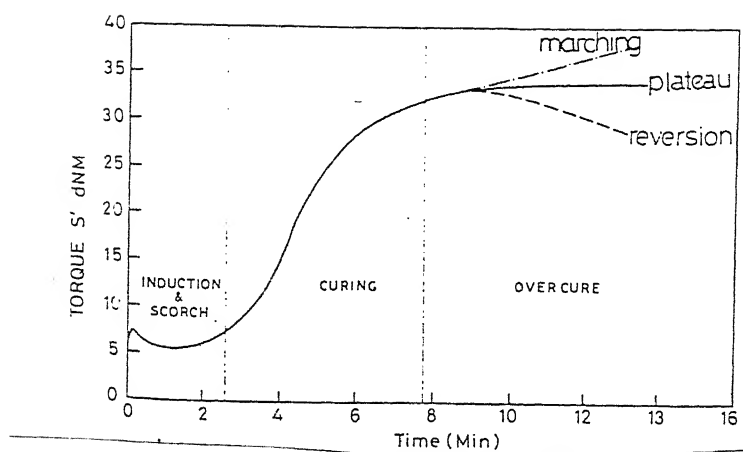


Fig. 2.4: Rheometer curve for vulcanization

2.4.1 Onset of Vulcanization : Induction and Scorch

This is the point of time at which the compound first begins to soften, thus becoming incapable of flowing thermoplastically; in the case of a press cure it is the point of time at which the compound ceases to flow in the mould. Depending on the vulcanization auxiliaries (additives) chosen, it may occur early (as with ultra-accelerators) or late (as with sulfenamides). With press curing the compound should be allowed to flow for a relatively long time before the onset of vulcanization in order that the cavities will be filled entirely, but in the case of open cure the earliest possible onset of vulcanization in order that the article to be vulcanized will help retain the article its original shape as closely as possible. It is also obvious that a later onset of vulcanization reduces the tendency to scorch during processing and raises the temperature which can be applied without a risk of scorching during compounding and shaping operations.

2.4.2 Curing

The region can be subdivided into undervulcanization and optimum vulcanization

2.4.2.1 Undervulcanization

This is the stage between the onset of vulcanization and the vulcanization optimum. It is the stage at which the torque still increases very much with the vulcanization time. As the degree of crosslinking is still small at this stage, most of the properties required in a rubber article are not achieved that a highly undervulcanized article is of no technical value.

The tensile strength of such an article is low, its elongation at break still very high and its permanent set so large that a fingernail impression remains as a deformation. The resistance to aging of such vulcanizates is also poor.

2.4.2.2 Vulcanization Optimum

In most cases goods have to be vulcanized to a fairly high degree of crosslinking - the vulcanization optimum. The technical vulcanization optimum is situated just below the maximum torque. This is because, when the vulcanization is continued upto the maximum torque or even beyond it, the products have relatively unfavourable aging properties.

2.4.3 Overcure : Plateau and Overvulcanization

The torque of most synthetic rubbers continues to rise slightly, yet continuously, after the vulcanization optimum, even when a long vulcanization time is chosen, and such rubbers are therefore said to have a "marching cure". But in the case of natural rubber, when the vulcanization optimum is exceeded the crosslinking is reversed at a rate which depends on the chosen vulcanization system and this "reversion" causes the mechanical properties to suffer. depending on how quickly the reversion takes place,

the curve is said to have a narrow or broad "plateau". The length of the plateau is a measure of the heat stability because it shows the influence of vulcanization heat on the mechanical properties. In some cases the curve proceeds almost parallel to the abscissa.

The shape of the plateau, which substantially determines the aging properties of a vulcanizate depends on the choice of vulcanization agents and the amounts in which they are employed. Reversion is caused by overlapping of two reactions: the crosslinking reaction and the depolymerizing reaction caused by the vulcanization temperature. The actual vulcanization curve results from the overlapping of the curves of these two reactions.

Following the onset of vulcanization the crosslinking proceeds at a rate which depends on the type and amount of accelerator.

When thermally very stable accelerators (e.g. guanidines and other basic accelerators) are used by themselves, the crosslinking versus the vulcanization time gives a curve (the dotted crosslinking curve in figure 2.5) which proceeds in a substantially linear manner at any rate where normal vulcanization times are concerned. Thus, as the vulcanization proceeds, a number of crosslinks are formed approximately proportional to the vulcanization time. When accelerators of lower thermal stability (e.g. thiurams) are used, the onset of vulcanization is followed at first by relatively fast crosslinking, which is indicated by a corresponding steep section of the crosslinking curve in figure 2.5. When a proportion of the accelerator becomes ineffective - owing to decomposition or deactivation of the radicals - and when the amount of free sulfur available for the crosslinking is reduced, the rate of vulcanization reduces. Accordingly curve (a), which shows formation of crosslinks becomes

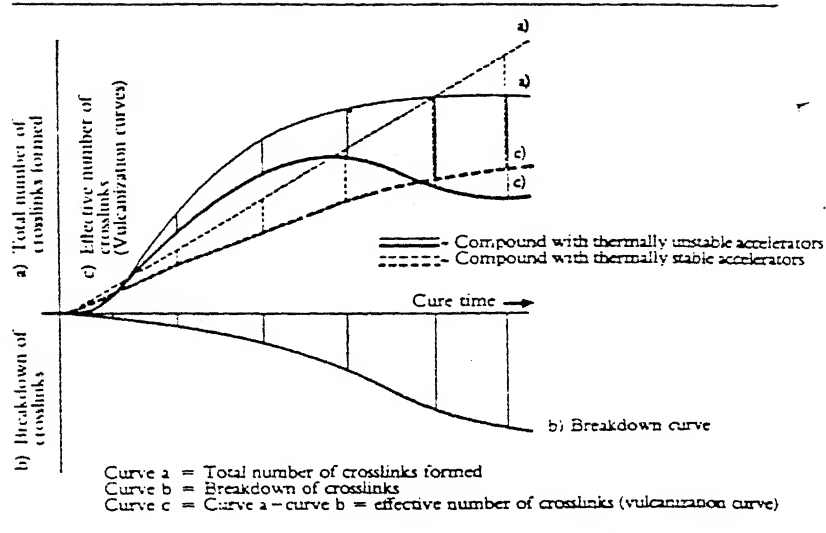


Fig. 2.5: Vulcanization curves for accelerators of varying stability. Reversion and rising characteristic of modulus. [Hofmann, 1967]

progressively flatter with the vulcanization time and finally proceeds asymptotically to the time axis. After a number of crosslinks have been formed during the vulcanization they can split up again by the vulcanization heat as the bond energy of sulfur crosslinks is smaller than that of hydrocarbon chains (Table 2.2), exclusively thermal splitting, i.e. splitting in the absence of oxygen, which takes place when goods are cured in a press, may be expected to result primarily in the breakdown of crosslinks. The split crosslinks, which are mainly radical in nature, are then capable of forming new crosslinks or, which occurs more frequently, of reacting intramolecularly.

Normally the splitting tendency of bridgelinks increases with the number of crosslinks. this is shown by curve (b) (depolymerization) in figure 2.5. If a high torque is obtained with only a small amount of sulfur (e.g. efficient vulcanization system), it may be

expected that the sulfur has been incorporated mainly in small fragments, primarily in the form of mono- or di-sulfidic links; but if a relatively large amount of sulfur (conventional vulcanization system) is required in order to achieve the same number of crosslinks, i.e. the same torque, it is likely that the bridges consist mainly of polysulfidic bonds.

Table 2.2: Bond energies of various types of crosslinks

Type of linkage	Bond energy (kcal/mol)
-C-S _x -C- Poly-sulfidic	<64
-C-S-S-C- Di-sulfidic	64
-C-S-C- Mono-sulfidic	68
-C-C- Hydrocarbon	84

Because the crosslinks differ from one another in their heat stability by reason of their chemical structure, those bridgelinks with the least heat resistance (or bond energy), i.e. the poly-sulfidic links, are the first to be broken down. When, after a fairly long vulcanization period, the majority of the most unstable crosslinks has been split up, further depolymerization takes place slowly, which is reflected in a bend in the depolymerization curve (curve b in figure 2.5). The overlapping of the fictitious crosslinking and depolymerization curves (a) and (b) gives vulcanization curve (c) in figure 2.5.

2.5 MECHANICAL PROPERTIES

2.5.1 Modulus

As long as the individual molecules of a rubber are not fixed to one another, especially at elevated temperatures, they can move more or less freely in relation to one another inside the mass (macrobrownian movement) the material is plastic. It shows mechanically and thermodynamically irreversible Newtonian flow and, within the range of its plasticity, it does not offer much resistance to a force acting upon it. The modulus is extremely small.

The larger the number of individual macromolecules bound together by the crosslinks in the course of vulcanization, the larger the force required to produce a given deformation and stiffer the vulcanizate. The force necessary to deform the material is often known as the "modulus". The correlation between modulus and the degree of crosslinking is given by [Hofmann,1967]:

$$f = \rho R T A_0^{-1} M_c^{-1} (\lambda - \lambda^{-2}) \quad (2.1)$$

f , modulus; ρ , density of rubber; R , gas constant; λ , elongation; A_0 , cross sectional area of the test specimen in the unstretched state; M_c , mean molecular weight of the rubber molecules situated between two crosslinks;

2.5.2 Hardness

As the degree of crosslinking rises, the hardness, similarly to the modulus, progressively increases until the material becomes ebonite. A constant deformation is produced when the hardness is measured; a needle or ball is used for this purpose and the force required to produce the deformation is indicated by a spring balance.

2.5.3 Tensile Strength

Unlike the modulus and hardness, the tensile strength passes through a maximum initially, after which, if the crosslinking is continued (in which case over-crosslinking takes place), it falls steeply. As the density of crosslinking increases, however, the tensile strength of some types of rubbers rises again sharply until it reaches that of ebonite. This trend can be explained by the phenomena of crystallization due to the orientation of the molecular chains. Most polymers when stretched undergo crystallization phenomena due to the orientation of the molecules. However, fairly large additions of sulfur, which are built in intramolecularly, deprive the rubber of its capacity for orientation and hence of its ability to become tougher when elongated. In rubbers which undergo little crystallizing orientation less reduction of the tensile strength is caused by over-crosslinking.

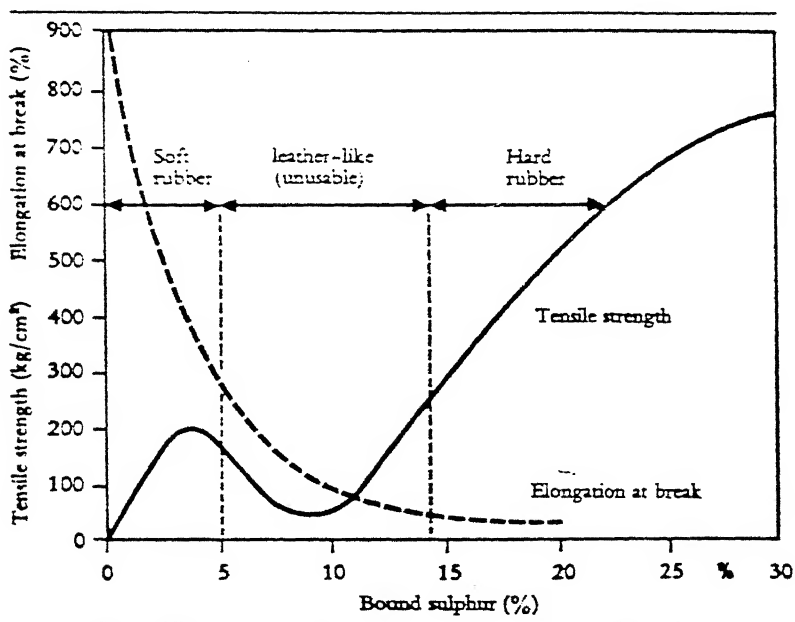


Fig. 2.6: Influence of bound sulfur content on tensile strength and elongation at break

When further sulfur is incorporated as a result of which all positions on the chains capable of crosslinking are finally bound by sulfur, the tensile strength again starts rising to previously unattainable levels. At this stage the tensile strength is due to purely chemical linkages, crystallization phenomena being excluded.

2.5.4 Elongation at Break and Compression set

As indicated in figure 2.6, the elongation at break decreases with increasing degree of crosslinking. It moves asymptotically in the direction of very small values.

The permanent set (e.g. tensile set, compression set) also becomes progressively smaller as the number of crosslinking positions increases. Therefore a high degree of crosslinking is always desirable in products which have to have a particularly low permanent set.

2.6 DYNAMIC MECHANICAL ANALYSIS

Polymers are usually described as viscoelastic materials, a generic term which emphasizes their intermediate position between viscous liquids and elastic solids. At low temperatures, or high frequencies of measurement, a polymer may be glass-like with a Young's modulus of 10^9 – 10^{10} Nm^{-2} and will break or flow at strains greater than 5%. At high temperatures or low frequencies, the same polymer may be rubber-like with a modulus of 10^6 – 10^7 Nm^{-2} , withstanding large extensions (~100%) without permanent deformation. At still higher temperatures, permanent deformation occurs under load, and the polymer behaves like a highly viscous liquid. Elastic materials have a capacity to store mechanical energy with no dissipation of energy; on the other hand, a viscous fluid in a nonhydrostatic stress state has a capacity for dissipating energy, but none for storing it.

When polymeric materials are deformed, part of the energy is stored as potential energy and part is dissipated as heat. The energy dissipated as heat manifests itself as mechanical damping or internal friction. The internal friction of materials is important, not only as a property index, but also for environmental and industrial applications. Since noise is radiated by the vibration of an object especially metallic materials, which have small internal friction (0.001-0.004) the application of damping materials to the vibrating surface will convert the energy into heat, which is dissipated within the damping materials rather than being dissipated as airborne noise. Amorphous viscoelastic polymers are good damping materials, having high internal friction (0.1-0.3). High damping or internal friction is essential in decreasing the effect of undesirable vibration, in reducing the amplitude of resonance vibrations to safe limits, and in all kinds of structures from airplane to buildings.

The commonly used dynamic mechanical instruments measure the deformation of a material in response to vibrational forces. The dynamic modulus, the loss modulus, and mechanical damping (internal friction) give the amount of energy dissipated as heat during the deformation.

The investigation of dynamic modulus and internal friction over a wide range of temperatures and frequencies has proven to be very useful in studying the structure of high polymers and variations of properties in relation to end use performance. These dynamic parameters have been used to determine the glass transition region, relaxation spectra, degree of crystallinity, molecular orientation, crosslinking, phase separation, structural or morphological changes resulting from processing, and chemical composition in polyblends, graft polymers, and copolymers.

2.6.1 Principles of Dynamic Mechanical Analysis

Dynamic mechanical analysis involves the determination of the dynamic mechanical properties of polymers and their assemblies. As a result of this analysis, the relationships between the dynamic properties and the structural parameters (crystallinity, molecular orientation, molecular weight, crosslinking, copolymerization, and plasticization, etc.) and environmental or external variables (temperature, pressure, time, frequency, type of deformation, surrounding atmosphere, humidity, etc.) can be explained.

In order to determine the dynamic mechanical properties (such as the dynamic modulus E' , the loss modulus E'' , and the damping or internal friction $\tan \delta = E''/E'$), various vibrational methods are used in nondestructive tests. These methods measure the response (deformation) of a material to periodic forces. Thus, the vibrational parameters - amplitude, frequencies, type of oscillation and wave propagation- become important in this analysis.

Different classes of vibrations like free vibrations; resonance vibrations; wave propagation; and sinusoidal excitation and response are used in the dynamic mechanical analysis [Murayama,1978]. In viscoelastic studies of polymeric materials the method of sinusoidal excitation and response is very useful. In this case, the applied force and the resulting deformation both vary sinusoidally with time, the rate usually being specified by the frequency f in cps or $\omega = 2\pi f$ in radians/s. For linear viscoelastic behaviour, the strain will alternate sinusoidally but will be out of phase with the stress as shown in figure 2.7. This phase lag results from the time necessary for molecular rearrangements and is associated with relaxation phenomena. The stress (σ) and strain (ϵ) can be expressed in complex notation as follows :

$$\sigma = \sigma_0 \sin (\omega t + \delta) \quad (2.2)$$

$$\varepsilon = \varepsilon_0 \sin (\omega t) \quad (2.3)$$

where ω is the angular frequency, and δ is the phase angle. Then

$$\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \quad (2.4)$$

$$E' = \sigma_0 / \varepsilon_0 \cdot \cos \delta \quad \text{and} \quad E'' = \sigma_0 / \varepsilon_0 \cdot \sin \delta, \quad (2.5)$$

where E' is the real part of the modulus and E'' the imaginary part. The complex representation for the modulus as shown in figure 2.7 can be expressed as follows:

$$\sigma = \sigma_0 \exp i(\omega t + \delta) \quad (2.6)$$

$$\varepsilon = \varepsilon_0 \exp (i\omega t) \quad (2.7)$$

Then

$$\sigma/\varepsilon = E^* = \sigma_0 / \varepsilon_0 \cdot \exp (i\delta) = \sigma_0 / \varepsilon_0 \cdot (\cos \delta + i \sin \delta) = E' + i E'' \quad (2.8)$$

and the phase angle δ is given by

$$\tan \delta = E'' / E' \quad (2.9)$$

$$E' = |E^*| \cos \delta \quad \text{and} \quad E'' = |E^*| \sin \delta \quad (2.10)$$

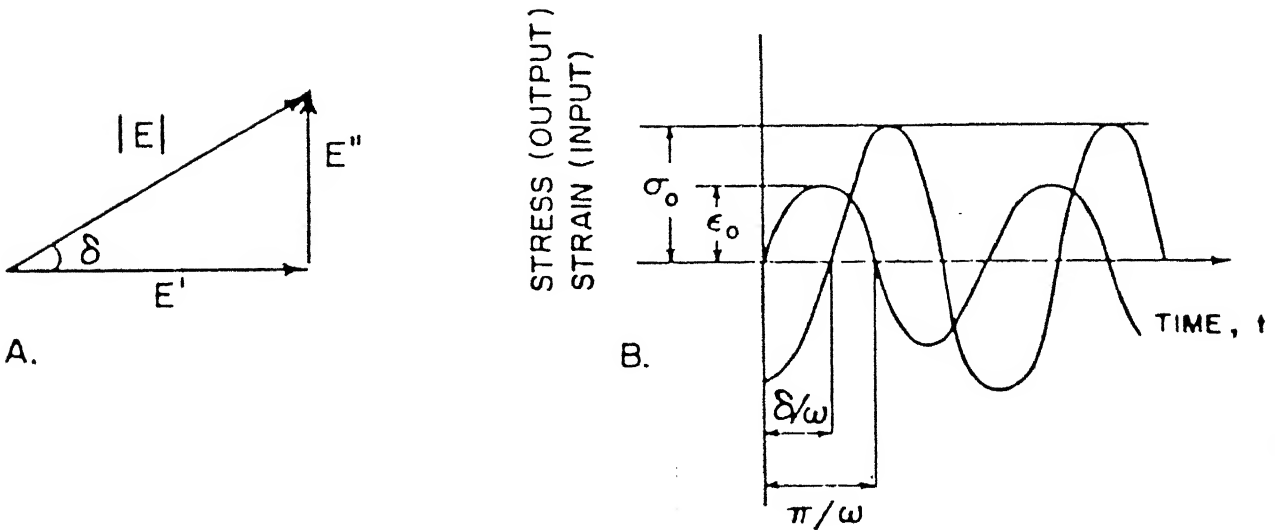


Fig. 2.7: Relations between various parameters used to express the results of a dynamic mechanical measurement

The real part of the modulus E' is called the storage modulus, because it is related to the storage of energy as potential energy and its release in the periodic deformation. the imaginary part of the modulus, E'' is called the loss modulus and is associated with the dissipation of energy as heat when the materials are deformed.

The stress or strain amplitude and the frequency are related in the heat generation in the polymeric material during oscillation $Q = \pi E'' \epsilon_0^2$, where Q is the heat dissipated per cycle, ϵ_0 the maximum value of the strain amplitude during a cycle and E'' the loss modulus.

Thus, the heat generation in a material is proportional to the square of the amplitude, to the frequency, and to the loss modulus. If a polymeric material is subjected to high frequency, high amplitude oscillations, the temperature of the specimen is increased. For example energy losses in the rubber compounds and in the fabric of tyre under dynamic loading result in drag component manifesting itself in internal heat generation which is readily observed as an increase in temperature above ambient.

Internal heat generation by oscillation is also a cause of structural changes in the polymers. Therefore in the determination of dynamic mechanical properties low levels of strain amplitude and low frequencies are often used. This low strain amplitude is in the linear region of the stress-strain curve.

2.6.2 Glass transition temperature

The properties of polymers change with temperature. In particular, it has been found that the coefficients of thermal expansion of amorphous polymers undergo abrupt changes in the region of the glass transition. The temperature at this abrupt change is defined as the glass transition temperature T_g .

Many amorphous polymers are hard rigid glasses below the glass transition temperature T_g . This is the glassy region where the modulus is greater than 10^{10} dyne/cm². In this glassy region, thermal energy is insufficient to surmount the potential barriers for translational and rotational motions of segments of the polymer molecules. The chain segments are frozen in fixed positions. Above the glass transition temperature, the amorphous polymer is soft and flexible. The modulus in this rubbery region is about 10^7 or 10^6 dyn/cm². Thus the modulus change between the glassy state and the rubbery state is about four orders of magnitude. This remarkable reduction of modulus is due to the initiation of micro-Brownian motion of the molecular chains from the frozen state with increasing temperature. The thermal energy becomes comparable to the potential energy barriers to segment rotation.

In the glass transition region, the polymer has short-range diffusional motion along with micro-Brownian motion. Segments are free to move from one lattice site to another, and the hard polymer becomes soft and rubbery.

The mechanical properties of the polymer change in the neighbourhood of the polymer. In dynamical mechanical studies, the dynamic modulus (storage modulus) decreases rapidly, and the loss moduli and $\tan \delta$ exhibit a maxima. This is one of the methods for the measurement of glass transition temperature T_g .

CHAPTER 3

SCOPE AND OBJECTIVE OF THE PRESENT WORK

Rubber compounds (elastomers) find varied usage in rocketry and space applications. They are frequently being used as thermal insulators, liner material between propellant and rocket motor insulation, putty for sealing joints between rocket motor segments to block hot gas leakage path, etc. They are employed as rubber pads bonded to metal shims in flexible joint of the movable nozzle of a solid rocket motor. They find application as bladders for storing liquid propellants for reaction control system of satellites. Our attempt in the present work is to develop a rubber compound suitable for use as compression gaskets, O-rings, hermetic seals, dust seals and vibration isolators at low temperatures encountered by upper stages of Space Launch Vehicles.

For the rubber compound to perform its intended functions reliably, the mechanical properties and the glass transition temperature, T_g are of primary importance. The mechanical properties of elastomeric compounds are evaluated in terms of tensile strength, elongation, modulus, compression set, hardness and dynamic behaviour - storage modulus and loss tangent. These properties are largely governed by the type of base rubber and the composition and the type of compounding ingredients like sulfur, accelerator, filler, plasticizer etc.

In this report, statistical techniques like design of experiments and response surface methodology would be applied to generate models for the mechanical properties, contours would be plotted for these model response equations to select the composition of the rubber compound which would yield the optimum properties. The

advantage of this technique is that the number of experimental compounding trials is limited to the minimum whereas information gained from the experiments is maximum. We would begin with identifying the ingredients (predictor-variables) that affect the mechanical properties of interest, followed by the selection of an efficient design of experiments. Compounding trials would then be taken up at the predetermined experimental points. The properties of the resulting rubber compounds would be characterized using standard ASTM methods. These would then be modeled using linear regression analysis (least squares method) and the response equations plotted as contours and response surfaces to select the rubber compound composition yielding the optimum properties of interest.

The variation in stress-strain characteristics and dynamic behaviour of rubber compounds with change in the vulcanization system (sulfur/accelerator ratio) and also the change in filler loading level would also be investigated. Glass transition temperature T_g for these compounds have also been determined.

Response surface methodology has found wide application in chemical process industry for optimizing yield of chemicals. But it has been put to limited use so far in optimizing rubber compound compositions, as trial and error method and one variable at a time (OVAT) approach are still in vogue in most rubber industries in our country and the world over. The use of RSM in developing Low Styrene-butadiene rubber compounds for low temperature applications will be demonstrated.

CHAPTER 4

EXPERIMENTAL PROCEDURES

4.1 MATERIALS

Selection of base rubber

Our aim is to develop a rubber compound which could be moulded into products like O-rings, gaskets, dust seals, vibration isolator pads etc. suitable for use at low temperatures ($\sim -50^\circ\text{C}$). Rubbers which can be used for low temperature applications should necessarily have a low glass transition temperature (T_g). Accordingly the options available are :

	T_g ($^\circ\text{C}$)
Natural rubber	-73 to -53
Styrene-butadiene rubber	-50
Polybutadiene rubber	-95
EPDM	-50

Easy availability and low cost were the prime considerations for beginning work with low styrene-butadiene rubber (LSBR) for our purpose. Also that styrene-butadiene rubber has better aging properties compared to natural rubber [Barlow, 1988].

The glass transition temperatures of styrene-butadiene copolymers vary almost linearly with the monomer ratios in the polymer. Since polystyrene has a T_g of about $+90^\circ\text{C}$ while that of polybutadiene is about -90°C it follows that the glass transition temperature of SBR with styrene content lower than 23% (normal grade) would be less than -50°C .

Accordingly low styrene SBR (styrene content 6-10%) manufactured by cold emulsion process under the trade-name SYNAPRENE-0212 was procured for R&D work from M/s. Synthetics and Chemicals, Bareilly .

Vulcanization system

Sulfur was preferred over Peroxide curing system. This is because Peroxides are rather hazardous chemicals and require more attention for safe storage and handling [Barlow,1988]. Peroxides also produce unpleasant odours during curing and in the vulcanizate. They react more readily with other compounding ingredients compared to conventional sulfur curing systems.

Sulfur was procured from M/s. Calichem, Germany (brand name crystex); specific gravity: 2.0 ± 0.1 ; assay: 90%; acidity: 0.15%; insoluble: 99% .

Accelerator system

Sulfenamide accelerators in the sulfur vulcanization of unsaturated rubbers results in a longer scorch but a more rapid rate of cure. CBS and TBBS give the maximum rate of cure amongst the sulfenamides. An excessively early onset of vulcanization is undesirable because it would impair the processing safety of the compound. It is also obvious that a later onset of vulcanization reduces the tendency to scorch during the processing and raises the temperature which can be applied without a risk of scorching during the compounding and shaping. The use of compounding ingredients like carbon black necessitate high processing temperatures which is possible only when the compound is adjusted to a sufficiently late onset of vulcanization. Thus it is necessary to use accelerators with a delayed onset of vulcanization, e.g. sulfenamide accelerators [Hofmann,1967]. Sulfenamides also result in better aging properties of the vulcanizates because of the predominance of mono-sulfide and di-sulfide bonds.

Moreover sulfenamides can be used as the sole accelerator in the semi EV and EV systems avoiding the use of a secondary accelerator thus making the design of experiments simpler.

CBS (N-cyclohexyl-2-benzo-thiazolesulfenamide) has been used as the sole accelerator for our trials. This was obtained from M/s. ICI India, Madras. The CBS was tested for: sp gravity, 1.27-1.32; M.P., 106 °C and ash content, 0.5%.

Other chemicals used are

Cure activators :

ZnO was supplied by M/s. Rubo-Chem Industries Ltd., Kottayam. (Properties are: particle size, 4 microns; assay, 95% as ZnO; specific gravity, 5.7 ± 0.3).

Stearic acid was also supplied by M/s. Rubo-Chem Industries Ltd., Kottayam. (Properties are: purity by carboxyl value, 98% ; specific gravity, 0.96 ± 0.3 ; M.P., 68-70°C).

The **filler, Carbon black (GPF)**, was obtained from M/s. Carbons & Chemicals Ltd., Kochi. (Properties are: VM, 0.7%; average particle size, 1.3 micron; sp. gravity, 1.87)

Softener :

A better dispersion of carbon black is accomplished with Naphthenic oil. Moreover this oil has good compatibility with SBR. Thus we have used **Naphthenic oil**, which was procured from M/s. Numex Chemical Corporation, Mumbai. (Property is: specific gravity, 0.92 ± 0.05)

Antioxidant, 2,2,4-trimethyl-1,2-dihydroquinoline, (trade-name Accinox TQ) was obtained from M/s. ICI India, Madras. (Properties are: specific gravity, 1.08 ± 0.02 ; softening point, 74-80 °C; ash content, < 0.3% (at 800 °C)).

Age resistor and mould release agent, Paraffin wax was supplied by M/s. SD Chemicals, Trivandrum (Properties are: density, 0.92 ± 0.05 ; congealing point, 62-64 °C)

4.2 RUBBER COMPOUND FORMULATION

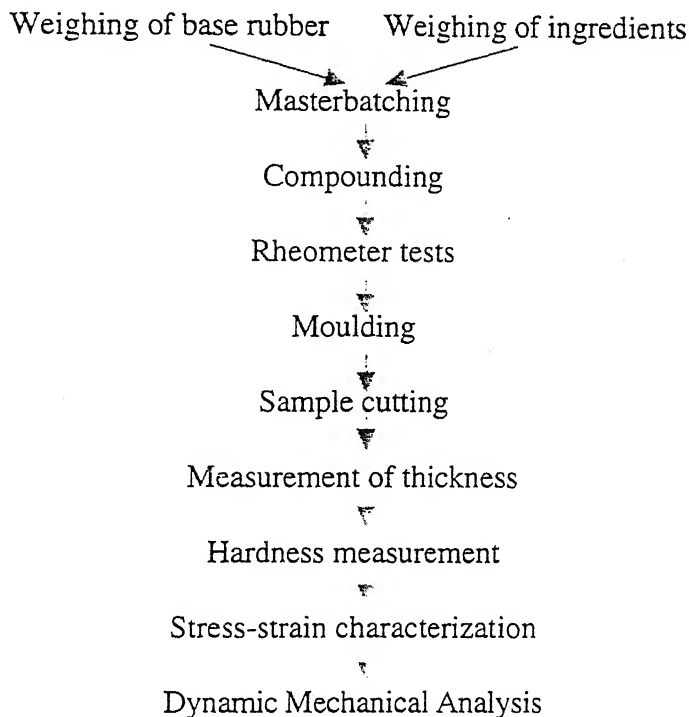
A masterbatch of composition as shown in table 4.1 was prepared, to which sulfur and CBS were added as per levels determined by the design of experiments. The filler loading (carbon-black level) was fixed at 70 phr from experimental trials conducted earlier, which gave a maximum tensile strength at this level as shown in table 5.6 in the next chapter (The only variable in this set of experimental trials was the level of filler, levels of all other ingredients were kept constant.). Levels of other ingredients have been fixed as per standard compounding practices.

Table 4.1: Rubber compound composition

Ingredient	phr
Low styrene SBR	100.0
Carbon black (GPF)	70.0
Zinc oxide	3.0
Stearic acid	1.0
Naphthenic oil	14.0
Accinox TQ	1.0
Paraffin wax	0.5
Sulfur	varied to design
CBS	varied to design

4.3 SEQUENCE OF OPERATIONS

The following sequence of operations was observed for preparing the rubber compounds and their characterization :



4.4 RUBBER COMPOUND PREPARATION

4.4.1 Masterbatching

Weighed quantity of raw rubber (LSBR) as per the recipe was masticated thoroughly on a 10 kg. capacity roll mill as shown in figure to get a smooth band of material around one of the rollers. This may be done by starting the roll mill with large nip and gradually reducing it during subsequent passes.

Once the band was formed, incorporation of weighed quantities of additives like ZnO, stearic acid, carbon black, naphthenic oil, accinox TQ and paraffin wax was done. While mixing, the band of material formed around one of rollers was periodically cut with a knife, folded and again fed on to the roll mill to get a homogenous mix of masterbatch. Around 6.5 kilograms of masterbatch was prepared in this operation.

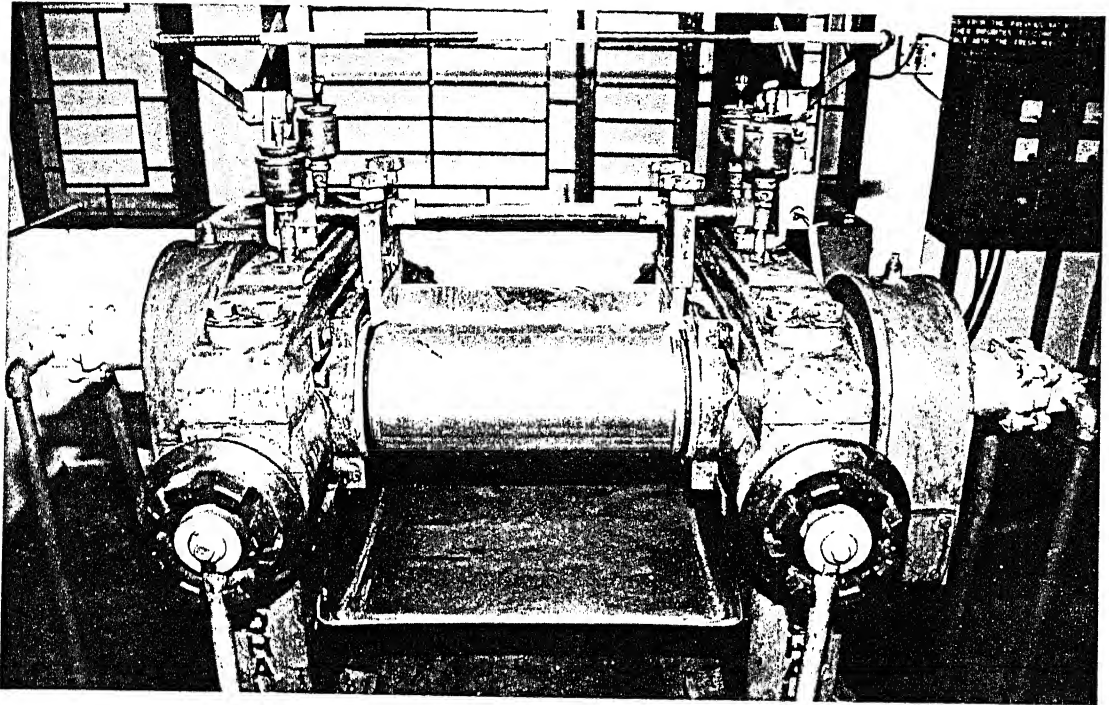


Fig. 4.1: Photograph of Laboratory roll mill

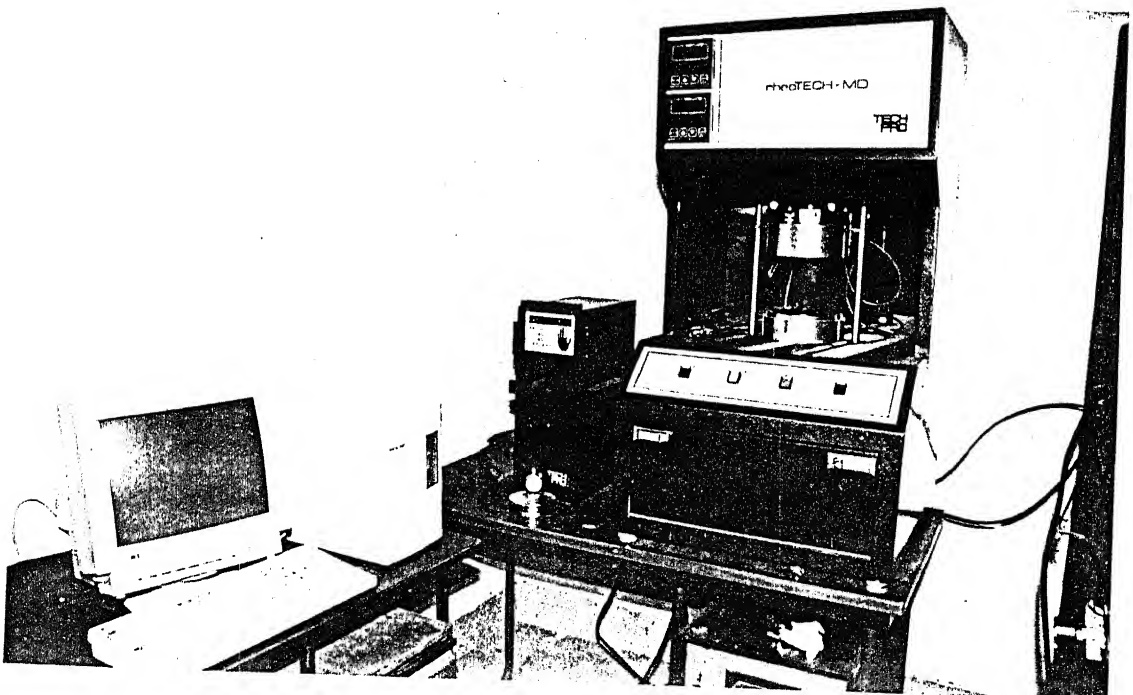


Fig. 4.2: Photograph of Rheometer

4.4.2 Compounding

The masterbatch was divided into 13 pieces of 473.7 gms each. These pieces were then individually masticated on a laboratory roll mill (fig. 4.1). Weighed quantities of sulfur and CBS as per the experimental design were added to each of these pieces of masterbatch so as to get the final raw rubber compound.

4.5 RHEOMETER : CURE TIME AND TORQUE

Rheometer (fig. 4.2) has been used to evaluate the cure-time and torque of the rubber compounds. Standard procedure used is ASTM D2084 and D5289. In this test the rubber is stretched to a given distance and then released at a set speed. The test is performed at an elevated temperature where the rubber can cure. The force required to stretch the rubber (torque) is directly proportional to the stiffness of the rubber. The shape of the rheometer curve can be thought of as a measure of the stiffness of the rubber with respect to time at curing temperature.

When a room temperature specimen is placed in the rheometer it shows a particular value of torque. As the specimen warms up the torque decreases. As cure begins (scorch), torque again increases. When curing is complete the torque levels off.

4.6 MOULDING, SAMPLE PREPARATION

Adequate quantity of raw rubber compound was weighed from each mix for moulding 2mm thick slab, 5mm thick slab and compression set buttons. The vulcanization press (fig. 4.3) was set for a cure temperature of 145°C and the mould was heated for 2-3 hours till stabilization. The rubber compound is then placed inside the mould and cured under

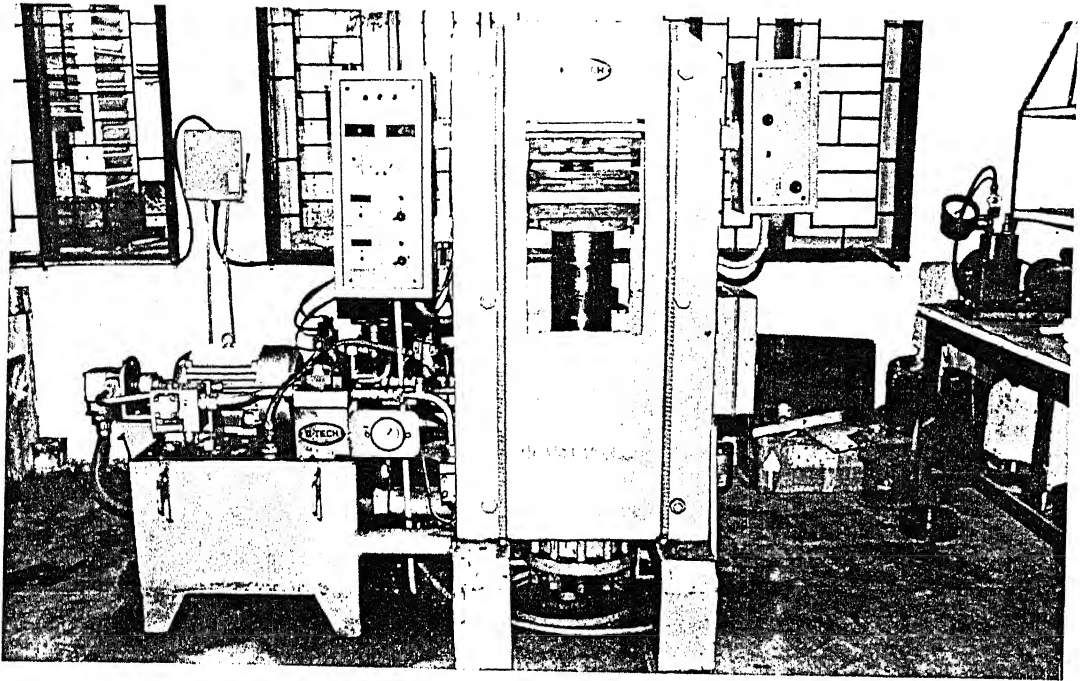


Fig. 4.3: Photograph of vulcanization press

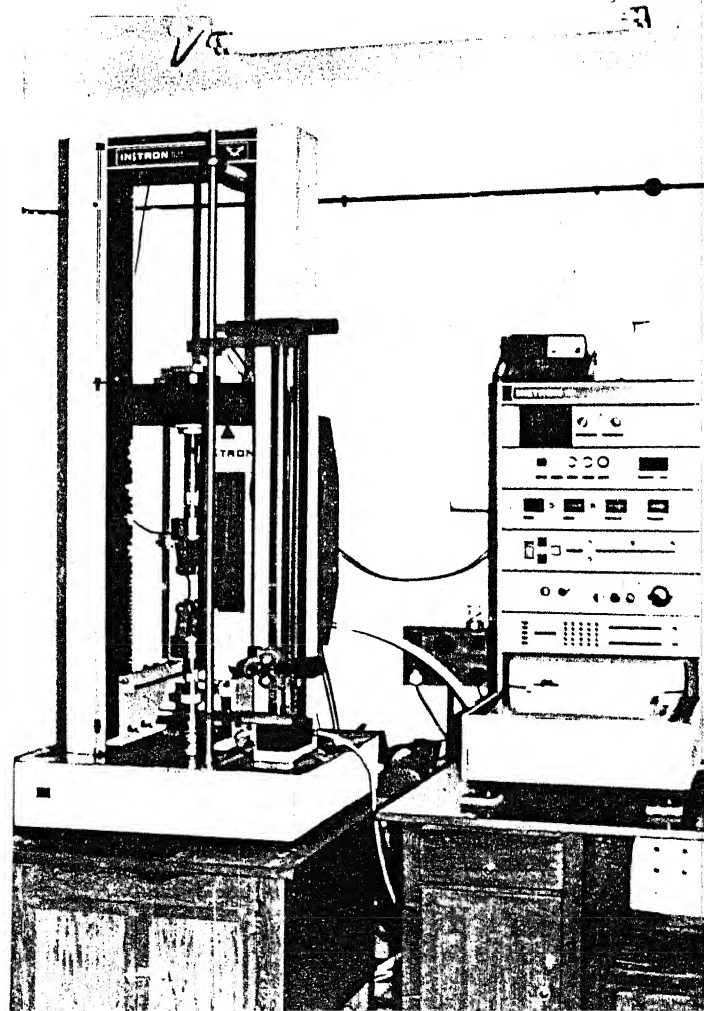
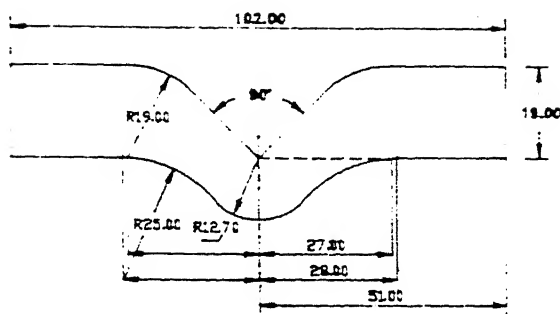
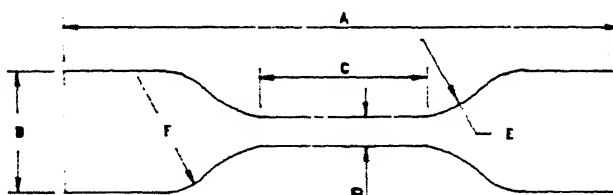


Fig. 4.4: Photograph of Instron 1121 testing machine



TEAR TEST SPECIMEN.



DUMBBELL SPECIMEN.

NOMENCLATURE	TYPE 1	TYPE 2
A	115.0	75.0
B	25.0 \pm 1.0	12.5
C	33.0 \pm 2.0	25.0 \pm 1.0
D	6.0 \pm 0.4	4.0 \pm 0.1
E	14.0 \pm 1.0	8.0 \pm 0.5
F	25.0 \pm 2.0	12.5 \pm 1.0
THICKNESS	2.0 \pm 0.2	2.0 \pm 0.2

Fig. 4.5: Tear and Dumbbell test specimens

pressure for a specified cure time as determined by cure time studies. Periodically the temperature in the mould is checked using thermocouple.

Dumbbell, tear and rheovibron test specimens are cut using respective dies. Compression set buttons are trimmed for flash. These are then measured for dimensions. Drawings of tear and dumbbell test specimens are shown in figure 4.5.

4.7 STRESS-STRAIN CHARACTERISTICS

ASTM D412 method has been employed for evaluating the stress-strain characteristics. The most commonly used method of mechanical characterization is the stress-strain measurement under tension. The specimen is extended at a uniform rate in a universal testing machine (Instron 1121), figure 4.4, and the resulting load on the specimen is continuously recorded as a function of time /extension. The ratio of maximum load required to break the specimen to the cross-sectional area is taken as the tensile strength of the material and expressed in ksc (kgf/cm^2) and the ratio of the extension at break to the original gauge length of the specimen is taken as the ultimate elongation and is usually expressed as % elongation. The load vs. extension curves can be converted into stress-strain curves by knowing the initial cross sectional area of the specimen and its effective gauge length. From the initial linear portion of the stress-strain curve the stress corresponding to a fixed strain is taken as a measure of the modulus of the material.

Instron 1121

The equipment (Instron 1121), figure 4.4, consists of a twin column load frame, a highly sensitive and accurate electronic load weighing system and a console mounted monitoring system. Depending on the requirement and load rating of the frame, load cell of the suitable range may be mounted on the moving cross head. Testing is carried

out with the lower end of the load string enclosed to the base beam and the upper end connected to the load cell using splittable specimen gripping arrangements and fixtures. The drive to the load screws and hence to the cross head is provided by a DC motor, and associated power amplifier built in the base unit. The commands to the crosshead drive motor are derived from the control console. Cross-head positional information and information regarding specimen performance during test is passed back to the console for control and display purposes. The control console provides communication between the operator, the machine frame and other devices for recording the test results.

The calibrated transducer (load cell) mounted at the centre of the moving cross-head measures the load applied on the specimen. The features of the load cell include a self identifying resistor which is a foil strain gauge and a pre-amplifier. The foil strain gauge consists of an etched foil intimately bonded to an elastic element which deforms slightly under applied load, causing change in resistance and hence imbalance in the wheatstone bridge circuit of which it forms an arm. the output is fed to a recorder to provide load-time or load-extension curves.

The dumbbell specimens conforming to ASTM D412 are used for stress-strain tests. Dumbbells are die cut from 2mm sheets moulded earlier, as to give defect free parallel cutting edges which eliminate stress concentration. Dumbbell specimens are preferred over the straight ones to avoid premature failure of the specimen at the grip.

The gripping of the specimen at its wider portions to prevent premature failure causes the non-uniform extension of its gauge length portion. The determination of effective gauge length (EGL) and calculation of strain based on that EGL gives more reliable strain values.

The use of elastomeric grips which ensure line contact and hence minimum slippage improves the quality of the strain measurement of elastomeric materials to a considerable extent. A crosshead speed of 500 mm/min was used for testing. The Instron 1121 was calibrated with the load cell of required range after the completion of successful self test. Input data like crosshead speed, load range and chart speed were given via keyboard entries in the control console. Dumbbell specimens were aligned properly in the elastomeric grips at a grip distance of 50mm and pulled at a fixed rate of 500mm/min.

4.8 HARDNESS

Hardness of a material is indicative of its elastic modulus. As the degree of crosslinking rises, the hardness progressively increases until the material becomes ebonite. The more compact the network, the shorter the molecular segments between the crosslinks, hence the tighter the network, which causes increased hardness. The indentation hardness value is inversely related to the penetration of an indenter of specific dimension into the material and is indicated in the calibrated dial of the durometer. It is expressed in shore A hardness (SAH) units,. The hardness test were performed as per the ASTM D2240

4.10 COMPRESSION SET

Compression set tests are intended to measure the ability of rubber compounds to retain elastic properties after prolonged action of compressive stresses. The actual stressing service may involve the maintenance of definite deflection, the constant application of a known force, or the rapidly repeated deformation and recovery resulting from intermittent compressive forces. The compression set tests are considered to be only those involving static stresses.

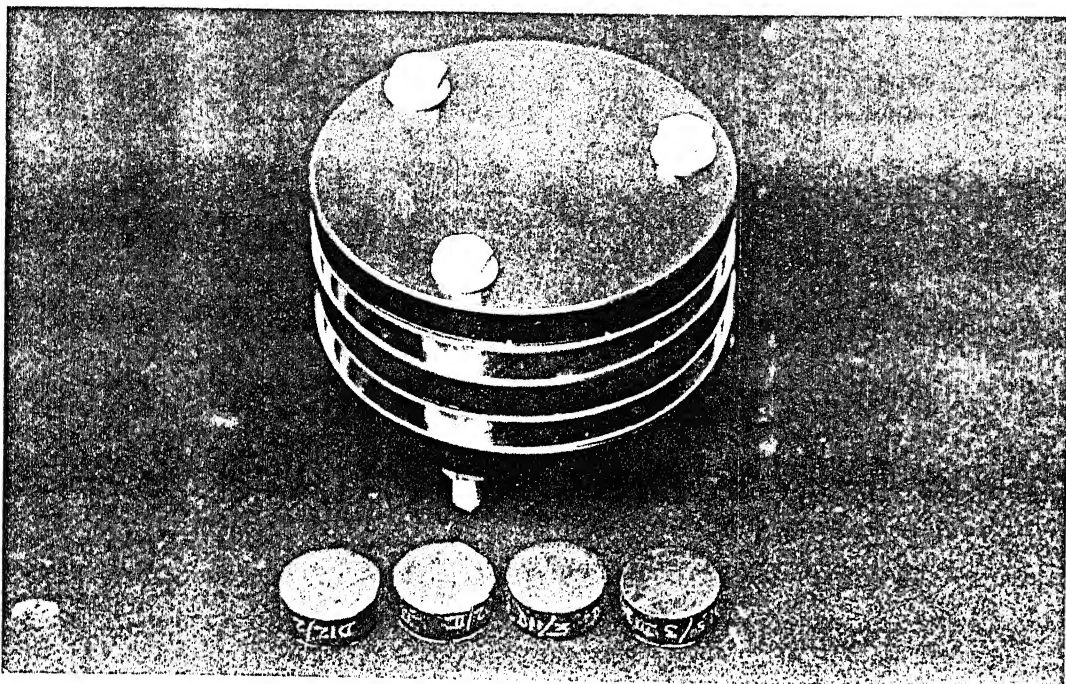


Fig. 4.6: Photograph of Compression set device and button specimens

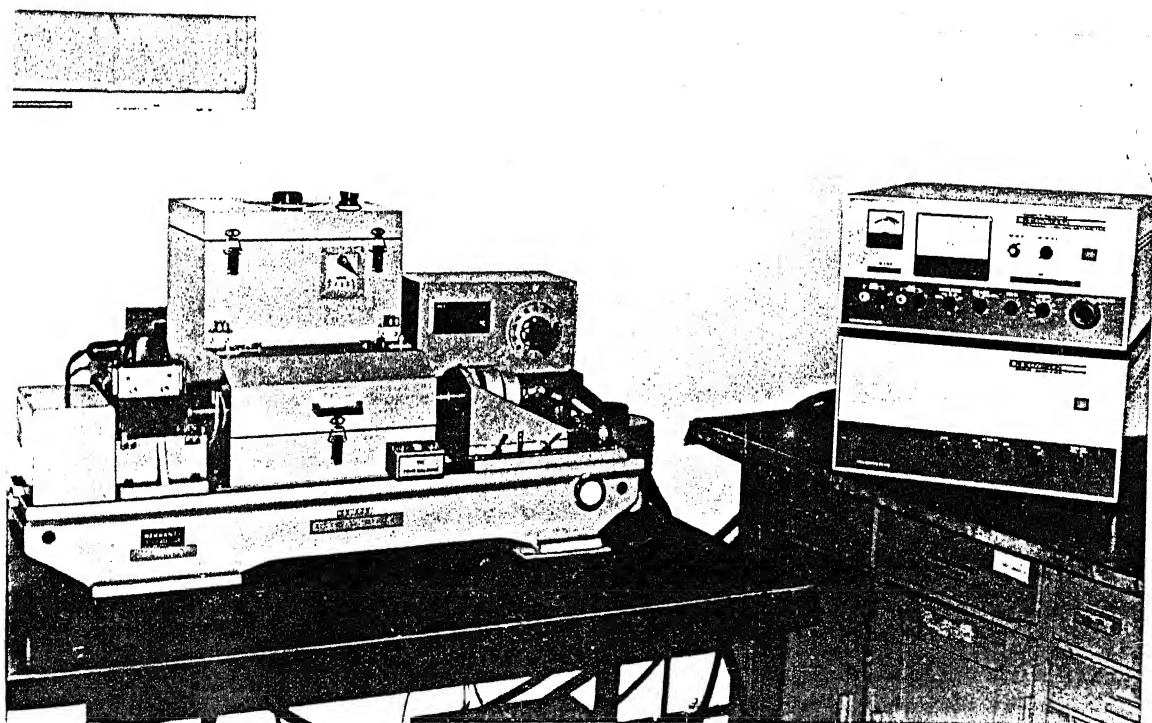


Fig. 4.7: Photograph of Rheovibron apparatus

Compression set tests were conducted as per ASTM procedure D395 using a compression set device and button specimens as shown in figure 4.6. The test specimens (compression set buttons) were placed between the plates of the compression device with the spacers in between. The bolts of the device were tightened so that the plates are drawn together uniformly until they were in contact with the spacers. The percentage of compression applied was 25%. The assembly was then placed in an oven at a specified temperature (70°C) for the required duration (24 or 72 hours). It was then removed from the oven and the specimens were released and measured for final thickness after 30 minutes cooling and stabilization period.

$$\text{compression set, \%} = [(t_0 - t_1)/t_1] \times 100$$

t_0 = original thickness of the specimen; t_1 = final thickness of the specimen

4.10 DYNAMIC MECHANICAL ANALYSIS

The **Rheovibron** (figures 4.7 and 4.8) is designed to measure the temperature dependence of the complex modulus (E^*), dynamic storage modulus (E'), dynamic loss modulus (E''), and dynamic loss tangent ($\tan \delta$) of viscoelastic materials at specified selected frequencies (0.01 to 1 Hz, 3.5, 11, 35 110 Hz) of strain input. It is unique because it was designed to read $\tan \delta$ directly, greatly simplifying and speeding the characterization of a material. The test is done as per ASTM procedure D2231. The Rheovibron was commercialized by Toyo Measuring Instruments Co.

During measurement, a sinusoidal tensile strain is imposed on one end of the sample, and a sinusoidal tensile stress is measured at the other end. The phase angle δ between strain and stress in the sample is measured by a direct-reading method. The instrument uses two transducers for detection of the complex dynamic modulus (ratio of maximum stress

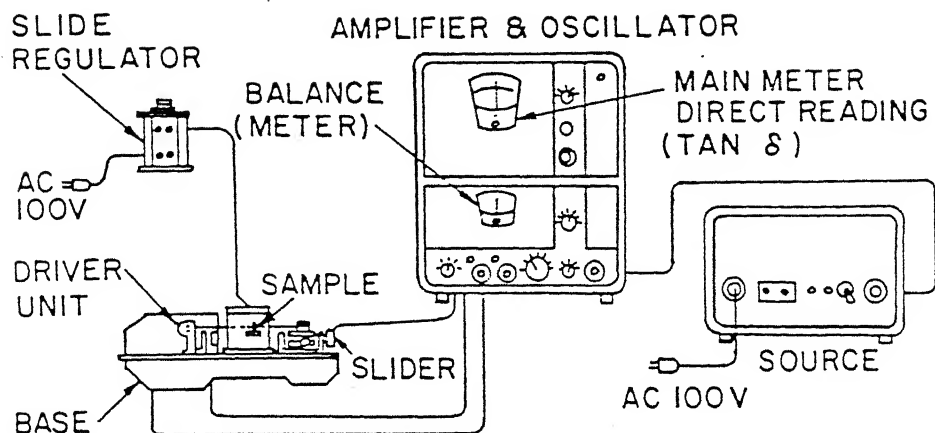


Fig. 4.8: Schematic drawing of a Rheovibron apparatus

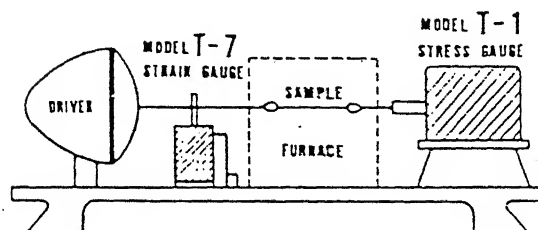


Fig. 4.9: Arrangement of transducers in a Rheovibron apparatus

amplitude to maximum strain amplitude) and the phase angle δ between the stress and strain. From these two quantities, the real part (E') and the imaginary part (E'') of the complex dynamic tensile modulus (E^*) can be calculated.

Figure 4.9 shows the arrangement of transducers and the location of sample. In this case, one end of the sample is driven at a certain frequency by means of a magnetic coil. The amount of strain or stress is transformed into an electrical quantity proportional to it by using an unbounded-type wire strain or stress gauge.

Operationally, the dynamic moduli are calculated as follows:

$$|E^*| = 2.0 \cdot L \cdot 10^{12} / (8 \cdot A \cdot D \cdot S) \text{ dynes/cm}^2 \quad (4.2)$$

L , length of the sample (cm); S , sample cross section (cm²); A , an instrumental constant obtained from the value of amplitude factor when measuring $\tan \delta$; D , the value of the dynamic force read from the dial when measuring $\tan \delta$.

E' and E'' can be calculated from the following equations:

$$E' = |E^*| \cos \delta \quad (4.3)$$

$$E'' = |E^*| \sin \delta = E' \tan \delta \quad (4.4)$$

CHAPTER 5

RESULTS AND DISCUSSIONS

The following section briefly gives the Response Surface Technique and the Design of experiments as applicable to the present Rubber compound optimization work. Once the compounds were processed as per the experimental design, the rheometer torque and cure time were evaluated from an average of 2 to 3 samples. The individual compounds were then press moulded and die cut or trimmed into standard testing specimens for characterization of mechanical properties. For evaluation of various properties like modulus (M-100), stress at 300% elongation (M-300), tensile strength, elongation, tear strength and hardness, an average of 6 to 7 samples was used. Likewise for evaluation of compression set at 70°C for 24 hr and 72 hr an average of 2 to 4 button samples has been used.

These properties were fitted by model equations using regression analysis. Contour diagrams and response surfaces have been plotted to determine the optimum compound composition. Effect of change in vulcanization system and filler loading on stress-strain characteristics and dynamic mechanical properties have also been studied.

5.1 RESPONSE SURFACE METHODOLOGY

The goal of most experimentation is to characterize the relationship between a response and a set of factors of interest to the researcher. This is accomplished by constructing a model that describes the response over the applicable ranges of the factors of interest. The old standard in scientific experimentation was to hold all but one variables constant while methodically changing one at a time. This method would eventually lead to conclusions about the effect of each variable while totally neglecting

any multiple variable interactions usually leading to false conclusions. The efficiency of experimental design can be appreciated in the identification of these interactions as well as the required number of trials required to reach the desired conclusions.

This optimization study can be performed using Response Surface Methodology (RSM). It is elaborately discussed by Box et al, 1978; Davies, 1967; Gunst et al, 1989 and Montgomery, 1984.

Let Y be the response of a chemical process dependent on the levels of k factors (x_1, x_2, \dots, x_k) which can be precisely measured and controlled. The model for the u^{th} combination of factor levels is given by,

$$Y_u = \phi(x_{1u}, x_{2u}, \dots, x_{ku}) + \epsilon_u, \quad u = 1, 2, \dots, N \quad (5.1)$$

where, N is the number of experiments, ϕ is the functional relationship and ϵ is the error involved

A geometric portrait of the response function in the factor space is called a response surface. The experimental region R , is a bounded subspace of the whole factor space. This is necessary due to practical limitations. RSM locates a point (x_1, x_2, \dots, x_k) within the experimental region R , where Y is at an extreme for the experimental region.

There are several steps involved in the RSM procedure. Initially the predictor variables the variation of which have a significant influence on the response, are identified. Then the factor space within which these variables are to be changed is fixed. Next step is to design a set of experiments and execute them in order to achieve reliable estimates of the parameters. If there are a few factors involved, a factorial design can be used. Fractional factorial designs are necessary once the number of factors increases. Central

composite design and Box and Behnken designs are best suited near the optimum region.

The next step in RSM is to propose a suitable mathematical model to fit the experimental data using multiple linear regression. F-tests for model and lack of fit are conducted to test the adequacy of the model [Gunst,1989]. In addition to this the R^2 test can also be conducted. The final step is to find the optimum conditions of the predictor variables which will produce the maximum (or minimum) value of the response.

In a region remote from the optimum, little curvature is present and a first order model will be satisfactory to describe the response surface. In the vicinity of the optimum, however, the surface will have a curvature and higher order models will be required.

The sequence of steps of design, model fitting and search for optimum are repeated until the curvature is detected and a true optimum is reached. The method of steepest ascent is the usual method for approaching the optimum based on the adequate equation. A note to be considered is that the choice of the region to be studied will dictate the optimum found. An optimum may be global or it may be local.

5.2 DESIGN OF EXPERIMENTS

Designing experiments to study or fit response surfaces is important for several reasons

- the response function is characterized in a region of interest to the experimenter
- statistical inferences can be made on the sensitivity of the response to the factors of interest,
- factors levels can be determined for which the response variable is optimum (maximum or minimum), and
- factor levels can be determined that simultaneously optimize several responses if

simultaneous optimization is not possible, tradeoffs are readily apparent.

Several different types of designs are useful when one is attempting to fit a response surface. Complete and fractional factorial experiments in completely randomized designs are extremely useful when one is exploring the factor space in order to identify the region where the optimum response is located. When the region of optimum response has been located, curvature can be pronounced. Three-level factorial experiments are often conducted in order to fit such response surfaces.

As the number of factors increases, the 3^k factorials become inefficient and impractical. Further, these designs do not give equal precision for fitted responses at points (factor level combinations) that are at equal distances from the centre of the factor space. A design that has this property is termed a rotatable region. Rotatability is a desirable property for response surface models because prior to the collection of data and the fitting of the response surface, the orientation of the design with respect to the surface is unknown. Thus, the exploration of the response surface is dependent on the orientation of the design. A rotatable design can be constructed from equally spaced points (factor levels) on circles or a spheres.

5.2.1 Design Selection for Rubber Compounding Problems

The following broad criteria are to be satisfied by the design [Derringer, Rubber age, 1972]:

- a) The first requirement for a statistical design is that the number of experiments should be greater than or equal to the number of coefficients in the regressed model.
- b) It should allow the second degree polynomial (tentatively assumed to be representationally adequate) to be estimated with satisfactory accuracy within the region of interest

c) It should allow a check to be made on the representational accuracy of the fitted equation by including replicated points.

d) It should not contain an excessively large number of points. That is to say that the redundancy factor $R_f = N/p$ should not be excessively large, where N is the number of design points and p the number of coefficients to be estimated.

e) It should lend itself to blocking.

f) It should form a nucleus from which a satisfactory design of third degree can be built if the second degree polynomial proves inadequate.

g) It should be rotatable.

5.2.2 Central Composite Design

Central composite designs [Box and Hunter, 1978] are the best suited ones for rubber compounding problems because they meet most of the criteria mentioned above. The major fault with this type of design is that the redundancy factor may be considered excessive, especially in the 4 and 6 variable case. If cost is a critical factor the Hartley and Westlake designs [Derringer, Rubber age, 1972] can be employed.

Central composite designs (CCD), especially for 3 or more variables are generally run in blocks. CCD is an efficient rotatable design. The total number of design points in a CCD based on a complete 2^k factorial is $n = 2^k + 2k + m$ where k is number of factors and m the repeat observations at the design centre. For a design with two factors, the factor space would look like figure 5.1.

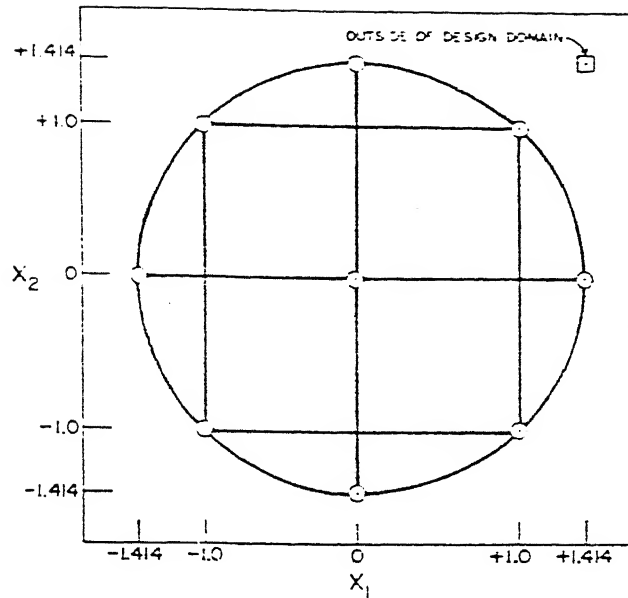


Fig. 5.1: Factor space of Central Composite Design with two factors

To begin with the experimentation the general scheme followed is:

Step 1: Factorial and a fraction of the centre points are run.

After obtaining the experimental data a linear model is fitted and it is tested for representational accuracy.

Step 2: Star points and remainder of centre points are run.

After obtaining the experimental data a quadratic surface is fitted and the quadratic model is tested for representational accuracy.

If after fitting the linear model in Step 1 an adequate fit is found, a move is made along the vector of steepest ascent to a point where higher response is predicted. Step 1 is repeated and ascending the path of steepest ascent continued until second order effects predominated. Then Step 2 is run to get a picture of the yield surface at its maximum.

In rubber compounding the experimental objectives are usually completely different. The rubber compounder is generally not in moving to an area of maximum properties. He usually knows exactly what area he is interested in (e.g. sulfur-accelerator studies) and he can usually expect the response surface to be quadratic. For most rubber studies then the following alternative approach is followed:

Step 1: Run Hartley or Westlake's design.

Experimental information is gained. Subsequently a quadratic model is fitted, and one or two degrees of freedom are available for testing representational adequacy if prior estimate of experimental error is available.

Step 2: After completing the design points in Step 1, run remainder of factorial points and centre points to complete the central composite design.

Using the additional experimental data a quadratic model is fitted with increased accuracy, and tested for representational accuracy from internal error estimate (replicated points).

In the present work we have proceeded in the following manner :

Selection of predictor variables

The degree of crosslinking and the type of links (mono-, di- and poly-sulfidic) determine the property of a rubber compound. As the degree of crosslinking rises, the hardness progressively increases until the material becomes ebonite. Likewise the modulus, tensile strength, tear strength, elongation, compression set and dynamic mechanical properties all are governed by the degree and type of crosslinking.

The most important ingredients affecting the degree and type of crosslinking are the sulfur and accelerator levels. By varying the sulfur to accelerator ratio, the types of crosslinks as well the crosslink density may be changed. For example, increasing the

accelerator dosage leads to better utilization of sulfur in the crosslink and produces shorter sulfur links.

Thus we have selected the curator (sulfur) and accelerator (CBS) as the predictor variables for our study.

Fixing of +/- levels for Predictor variables

The crosslink structure in a sulfur vulcanized rubber can be changed easily by changing the ratio of sulfur to accelerator. If the concentration of sulfur is high, a number of poly-sulfidic crosslinks ($C-S_x-C$, $x > 2$) can be achieved. The properties related to poly-sulfidic crosslinks (tensile strength, fatigue resistance, etc.) can be improved. With a low ratio of sulfur to accelerator and in the presence of sulfur donor, sulfur atoms are more efficiently utilized in the crosslinking reaction. Three different systems have been proposed in literature.

Conventional vulcanization, CV systems (high sulfur to accelerator ratio), where mainly poly-sulfidic links ($C-S_x-C$, $x > 2$) are formed. Efficient vulcanization, EV systems (low sulfur to accelerator ratio), where mono- and di-sulfidic crosslinks predominate. Semi EV systems , where the sulfur to accelerator ratio is between the conventional and EV systems.

The levels for the predictor variables i.e. sulfur and CBS as shown in table 5.1 have been selected so as to lie within the range of CV, semi EV and EV systems as proposed in literature [Brysdon,1988; Bhowmick,1994].

5.3 PROPERTIES OF LSBR COMPOUNDS FROM DESIGNED EXPERIMENTS (AT ROOM TEMPERATURE)

The properties as evaluated for the rubber compounds prepared from the design of experiments are tabulated below in table 5.3

Table 5.3: Response parameters

S.no.	Rheometer max. torque	Cure time	Ten sile strength	Elong ation at Break	Hardness	Modulus M-100	Stress at 300% eln. M-300	Tear strength	Compression set at 70°C	
									24hr	72hr
	(in-lb)	(min)	(ksc)	%	Shore A	ksc	ksc	kgf/ cm	%	
1	8.28	37.75	87.6	472.3	50	11.6	30.8	32.9	8.1	11.4
2	11.92	14.55	159.9	383.3	63	19.3	65.7	41.7	4.5	7.0
3	9.25	40.49	116.9	438.4	56	14.3	43.9	38.2	6.9	9.2
4	12.13	15.20	155.1	376.7	62	18.2	61.7	43.6	5.0	7.1
5	12.76	15.69	157.0	380.0	62	18.9	62.4	42.2	4.9	7.0
6	11.57	22.05	162.7	366.7	63	20.0	70.5	42.4	5.3	7.0
7	8.59	25.36	90.3	450.0	50	11.7	32.8	33.0	8.1	9.9
8	12.75	15.80	158.8	380.5	62	18.9	64.5	41.2	4.6	7.0
9	14.32	10.85	124.2	246.7	67	25.6	99.3	35.8	4.0	6.2
10	14.35	13.20	140.4	254.2	68	25.5	97.4	40.5	4.1	6.4
11	11.04	16.33	143.8	427.8	59	15.6	50.5	41.2	5.7	7.2
12	13.71	12.76	141.3	300.0	65	22.8	81.8	39.8	4.5	5.6
13	12.80	15.89	152.8	360.0	63	19.9	66.8	42.5	5.0	6.5

5.4 MODEL FITTING

After an experimental design is selected and the experiments run, the collected data were subjected to a multiple linear regression analysis. The coefficients are estimated by the well-known famous least squares technique.

$$\hat{B} = (X^T X)^{-1} X^T Y \quad (5.2)$$

where X is the design matrix, X^T is the transpose of the design matrix, Y is the vector of responses and B is the vector of coefficients. Details of this method are given by Box and Hunter, 1988.

There are several software available for conducting multiple linear regression. The output will generally include the coefficients for the response equation. For a design equation with two predictor variables the response equation with quadratic terms and interaction term included would look like :

$$\hat{Y} = b_0 + b_1 X_1 + b_2 X_2 + b_{11} X_1^2 + b_{22} X_2^2 + b_{12} X_1 X_2 \quad (5.3)$$

This response equation could be used for plotting contour diagrams or response surfaces.

In the present work the response equations (model fits) have been generated by regression analysis as described above using MATLAB (version 4.2) software. A quadratic model with first order interaction terms was assumed and found appropriate in all cases. The ANOVA tables and model adequacy tests for these models are presented in section 5.6. These response equations have been plotted as contours diagrams and response surfaces in figures 5.2 to 5.21.

1. Rheometer maximum torque (in-lb)

$$\hat{Y}_1 = 12.47 + 1.84 X_1 + 1.48 X_2 - 0.54 X_1^2 - 0.54 X_2^2 \quad (5.4)$$

2. Cure time T_{90} (min)

$$\hat{Y}_2 = 15.43 - 4.80 X_1 - 8.96 X_2 + 1.63 X_1^2 + 5.28 X_2^2 + 2.56 X_1 X_2 \quad (5.5)$$

3. Tensile strength (ksc)

$$\hat{Y}_3 = 156.72 + 15.80 X_1 + 6.53 X_2 - 18.85 X_1^2 - 11.97 X_2^2 - 23.68 X_1 X_2 \quad (5.6)$$

4. Elongation (%)

$$\hat{Y}_4 = 376.78 - 70.46 X_1 - 45.03 X_2 - 7.70 X_1^2 + 0.31 X_2^2 - 18.88 X_1 X_2 \quad (5.7)$$

5. Tear strength -Die C (kg/cm)

$$\hat{Y}_5 = 42.24 + 1.89 X_1 + 0.50 X_2 - 2.64 X_1^2 - 1.59 X_2^2 - 3.73 X_1 X_2 \quad (5.8)$$

6. Modulus M100 (ksc)

$$\hat{Y}_6 = 19.04 + 4.74 X_1 + 2.70 X_2 - 0.31 X_1^2 - 0.34 X_2^2 + 0.40 X_1 X_2 \quad (5.9)$$

7. Stress at 300% elongation M300 (ksc)

$$\hat{Y}_7 = 64.22 + 22.48 X_1 + 12.76 X_2 + 0.14 X_1^2 - 0.99 X_2^2 + 2.28 X_1 X_2 \quad (5.10)$$

8. Hardness (shore A)

$$\hat{Y}_8 = 62.40 + 5.81 X_1 + 3.22 X_2 - 1.70 X_1^2 - 0.95 X_2^2 - 1.25 X_1 X_2 \quad (5.11)$$

9. Compression set 24hr/70°C (%)

$$\hat{Y}_9 = 4.80 - 1.27 X_1 - 0.89 X_2 + 0.62 X_1^2 + 0.42 X_2^2 + 0.28 X_1 X_2 \quad (5.12)$$

10. Compression set 72hr/70°C (%)

$$\hat{Y}_{10} = 6.92 - 1.29 X_1 - 1.26 X_2 + 0.66 X_1^2 + 0.24 X_2^2 + 0.85 X_1 X_2 \quad (5.13)$$

5.5 ANALYSIS OF VARIANCE (ANOVA)

Analysis of variance takes the total variation in the response and determines how much of this variation is accounted for by the equation. The variation not accounted for by the equation is divided into variation due to model inadequacy (lack of fit) and variation due to experimental error.

Table 5.4: ANOVA table

Source of variation	Degrees of freedom	Sum of squares	Mean squares	$F_{\text{calculated}}$	$F_{\text{tabulated}}$
Model	p	SSR	$MSRG = SSR/p$	$F_{\text{model}} = MSRG / MSRS$	
Residual	n-p	SSE	$MSRS = SSE / (n-p)$		
lack of fit	n-p-g	SS_{LOF}	$MSL = SS_{\text{LOF}} / (n-p-g)$	$F_{\text{LOF}} = MSL / MSE$	
pure	g (no. of replicates-1)	SS_{PE}	$MSE = SS_{\text{PE}} / g$		
Total sum of squares	n	TSS			

For the response equation to fit adequately, the F_{model} should be significant and $F_{\text{lack-of-fit}}$ should be insignificant at 5% significance level. It is preferred that F_{model} should be 10 to 15 times greater than that required for bare significance level [Derringer, Rubber age,1972].

The Coefficient of determination, R^2 test

The coefficient of determination R^2 , is another extensively used measure of the goodness of fit of a regression model [Gunst,1989]. It is equal to the amount of variation of the response accounted by the equation divided by the total variation in the response. In short $R^2 \times 100$ is the percentage of total variation in the response which the equation explains.

$$R^2 = 1 - \text{SSE/TSS} \quad (5.14)$$

For least-squares estimates of the model parameters the value of R^2 lies between 0 and 1; the closer it is to 1, the closer the predicted responses are to the observed responses. The coefficient of determination is often adjusted to take account of the number of observations and the number of predictor variables. This adjustment is made because R^2 can be arbitrarily close to 1 if the number of predictor variables is too close to the number of observations. The adjusted R^2 is calculated from the following formula:

$$R_a^2 = 1 - a \cdot (\text{SSE/ TSS}) \quad (5.15)$$

$$\text{where } a = n / (n-p)$$

5.6 TEST FOR ADEQUACY OF THE MODELS (ANOVA)

5.6.1 Rheometer maximum torque (in-lb)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	114.65	19.11	119.44	3.87
Residual	7	1.12	0.16		
lack of fit	3	0.52	0.17	0.94	6.59
pure	4	0.70	0.18		
Total sum of squares	13	115.99			

$$R_a^2 = 1 - 13 \times 1.12 / (7 \times 115.99) = 98.21\%$$

Model is adequate

5.6.2 Cure time T_{90} (minutes)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	1052.84	175.47	108.99	3.87
Residual	7	11.28	1.61		
lack of fit	3	9.04	3.01	5.38	6.59
pure	4	2.24	0.56		
Total sum of squares	13	1064.51			

$$R_a^2 = 1 - 13 \times 11.28 / (7 \times 1064.51) = 98.03\%$$

Model is adequate

5.6.3 Tensile strength (ksc)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	7690.15	1281.69	43.67	3.87
Residual	7	205.46	29.35		
lack of fit	3	162.95	54.32	5.11	6.59
pure	4	42.51	10.63		
Total sum of squares	13	7895.61			

$$R_a^2 = 1 - 13 \times 205.46 / (7 \times 7895.61) = 95.17 \%$$

Model is adequate

5.6.4 Elongation (%)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	57772.75	9628.79	60.46	3.87
Residual	7	1114.82	159.26		
lack of fit	3	778.84	259.61	2.76	6.59
Pure	4	376.10	94.03		
Total sum of squares	13	58885.68			

$$R_a^2 = 1 - 13 \times 1114.82 / (7 \times 58885.68) = 96.48 \%$$

Model is adequate

5.6.5 Tear strength -die C (kg/cm)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	145.47	24.25	18.09	3.87
Residual	7	9.37	1.34		
lack of fit	3	6.08	2.03	2.48	6.59
pure	4	3.29	0.82		
Total sum of squares	13	154.85			

$$R_a^2 = 1 - 13 \times 9.37 / (7 \times 154.85) = 88.76 \%$$

Model is adequate

5.6.6 Modulus M-100 (ksc)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	240.07	40.01	102.59	3.87
Residual	7	2.74	0.39		
lack of fit	6	1.18	0.39	1.00	6.59
pure	4	1.56	0.39		
Total sum of squares	13	242.80			

$$R_a^2 = 1 - 13 \times 2.74 / (7 \times 242.80) = 98.63 \%$$

Model is adequate

5.6.7 Stress at 300% elongation M-300 (ksc)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	5374.51	895.75	243.41	3.87
Residual	7	25.76	3.68		
lack of fit	3	7.17	2.39	0.51	6.59
pure	4	18.59	4.65		
Total sum of squares	13	5400.34			

$$R_a^2 = 1 - 13 \times 25.76 / (7 \times 5400.34) = 99.11 \%$$

Model is adequate

5.6.8 Hardness (shore A)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	382.46	63.74	120.26	3.87
Residual	7	3.68	0.53		
lack of fit	3	2.48	0.83	2.77	6.59
pure	4	1.20	0.30		
Total sum of squares	13	386.31			

$$R_a^2 = 1 - 13 \times 3.68 / (7 \times 386.31) = 98.23 \%$$

Model is adequate

5.6.9 Compression set - 24 hr/70°C (%)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	22.96	3.83	63.83	3.87
Residual	7	0.43	0.06		
lack of fit	3	0.21	0.07	1.17	6.59
pure	4	0.22	0.06		
Total sum of squares	13	23.40			

$$R_a^2 = 1 - 13 \times 0.43 / (7 \times 23.40) = 96.59 \%$$

Model is adequate

5.6.10 Compression set - 72 hr/70°C (%)

Source of variation	Degrees of freedom	Sum of squares	Mean squares	F _{calculated}	F _{tabulated}
Model	6	32.18	5.36	117.32	3.87
Residual	7	0.32	0.05		
lack of fit	3	0.08	0.03	0.50	6.59
pure	4	0.24	0.06		
Total sum of squares	13	32.60			

$$R_a^2 = 1 - 13 \times 0.32 / (7 \times 32.60) = 98.17 \%$$

Model is adequate

In all cases we find that the model equation fits the experimental data very well. The R_a^2 test in most cases shows that more than 95% of the experimental data is fitting the respective equations. The F-test for model is significant and that for lack of fit is insignificant in all cases.

The model equations have been plotted as contour diagrams and response surfaces in figures 5.2 to 5.21.

5.7 DISCUSSIONS

5.7.1 Cure behaviour

It is evident from the contours in figure 5.2 that the **rheometer maximum torque** keeps increasing with the increase in the sulfur and CBS levels, whereas the cure time falls to a minimum of around 11 minutes at a combination of $S = 0.5-1.0$ and $CBS = 0.5-1.0$.

The rheometer torque value is governed by the number of crosslinks formed. When the amount of sulfur is low and that of accelerator is high, the sulfur is utilized efficiently in forming mainly mono- and di-sulfidic links.

When the level of accelerator is reduced keeping the level of sulfur constant, part of the sulfur gets consumed in forming poly-sulfide links thus reducing the degree of crosslinking and also the rheometer torque.

As the levels of sulfur and CBS are raised, large number of crosslinks are formed increasing the maximum torque value. When the level of sulfur is kept high but that of CBS is reduced the maximum torque again drops owing to inefficient utilization of sulfur in forming more number of poly-sulfide links thus reducing the total number of effective crosslinks in the compound.

Fig.5.2: Contour plots for rheometer maximum torque (in-lb)

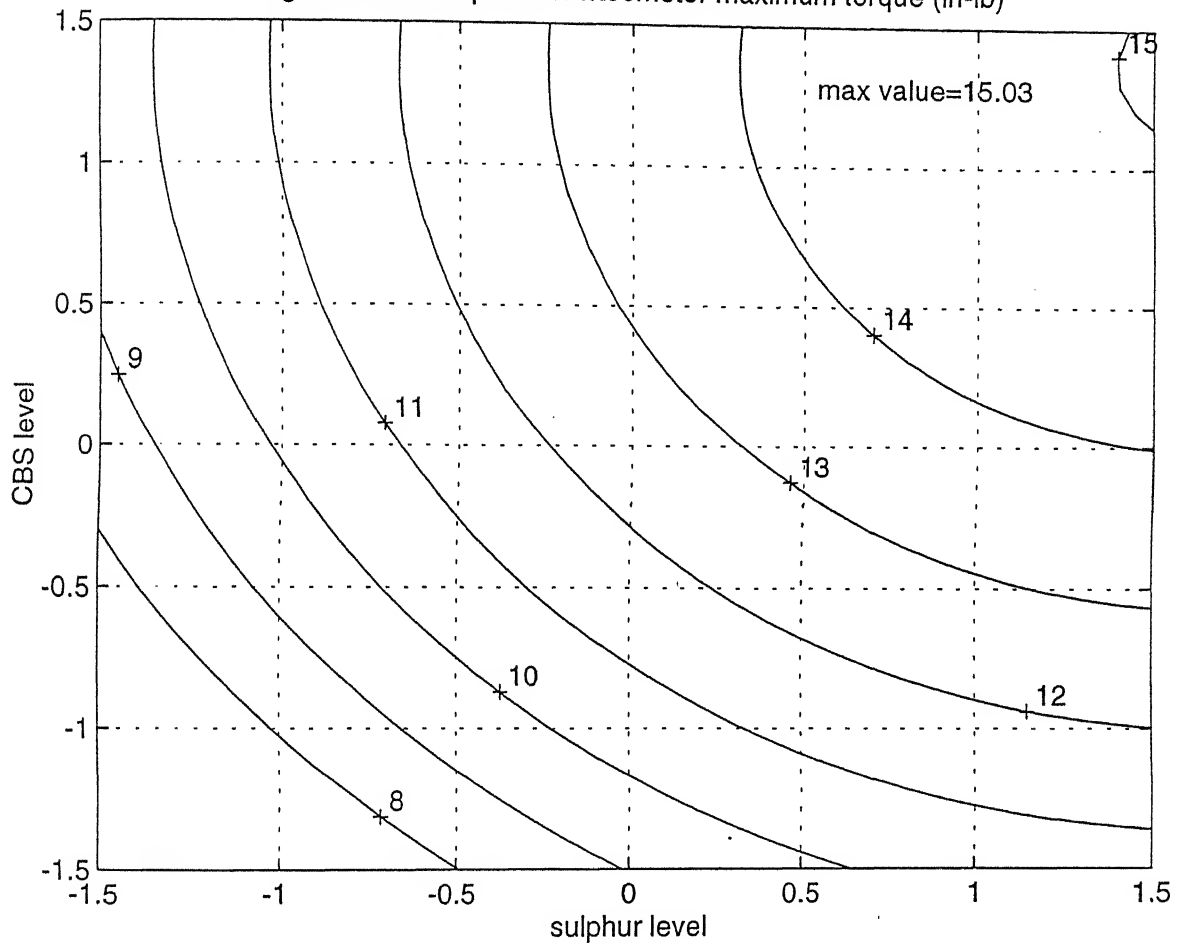


Fig.5.3: Response surface for rheometer maximum torque

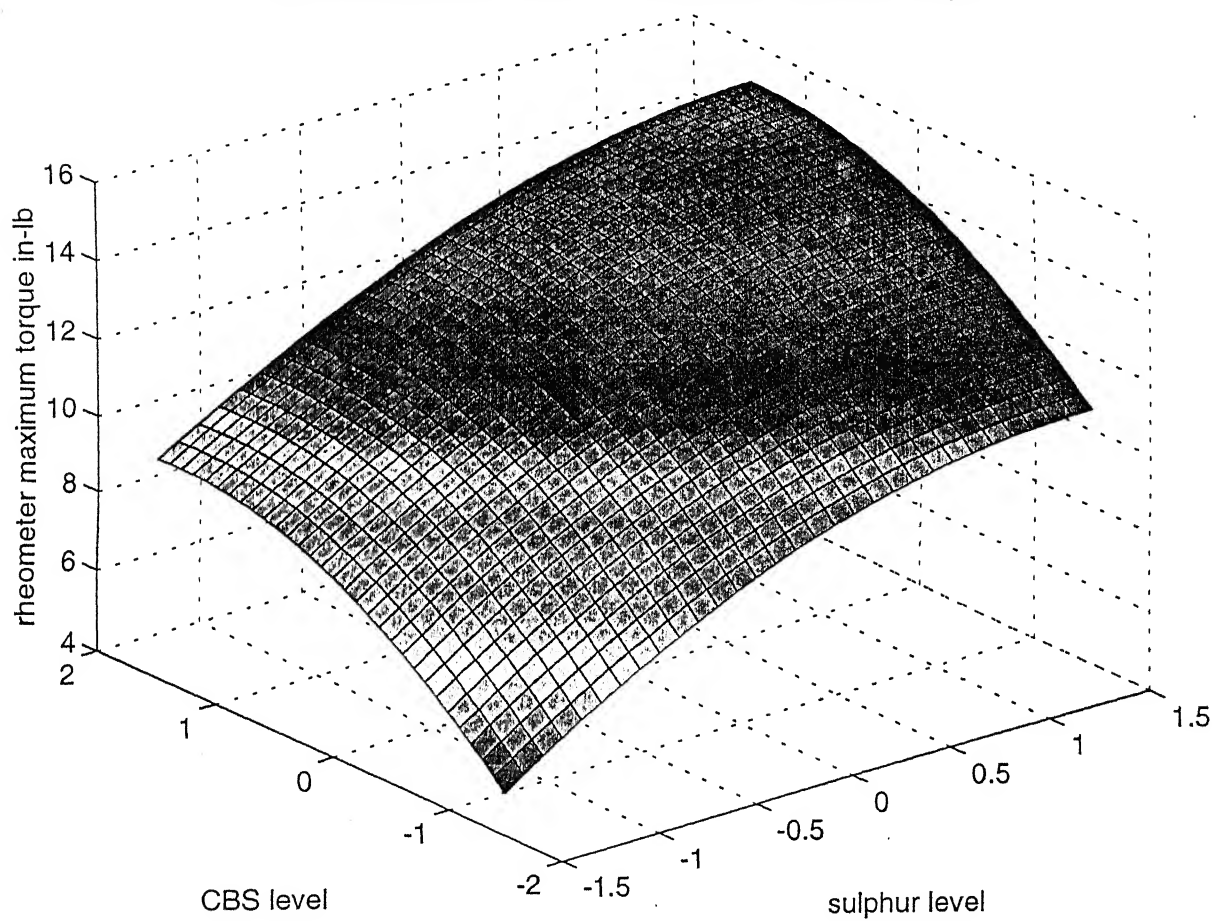


Fig.5.4: Contour plots for cure-time (minutes)

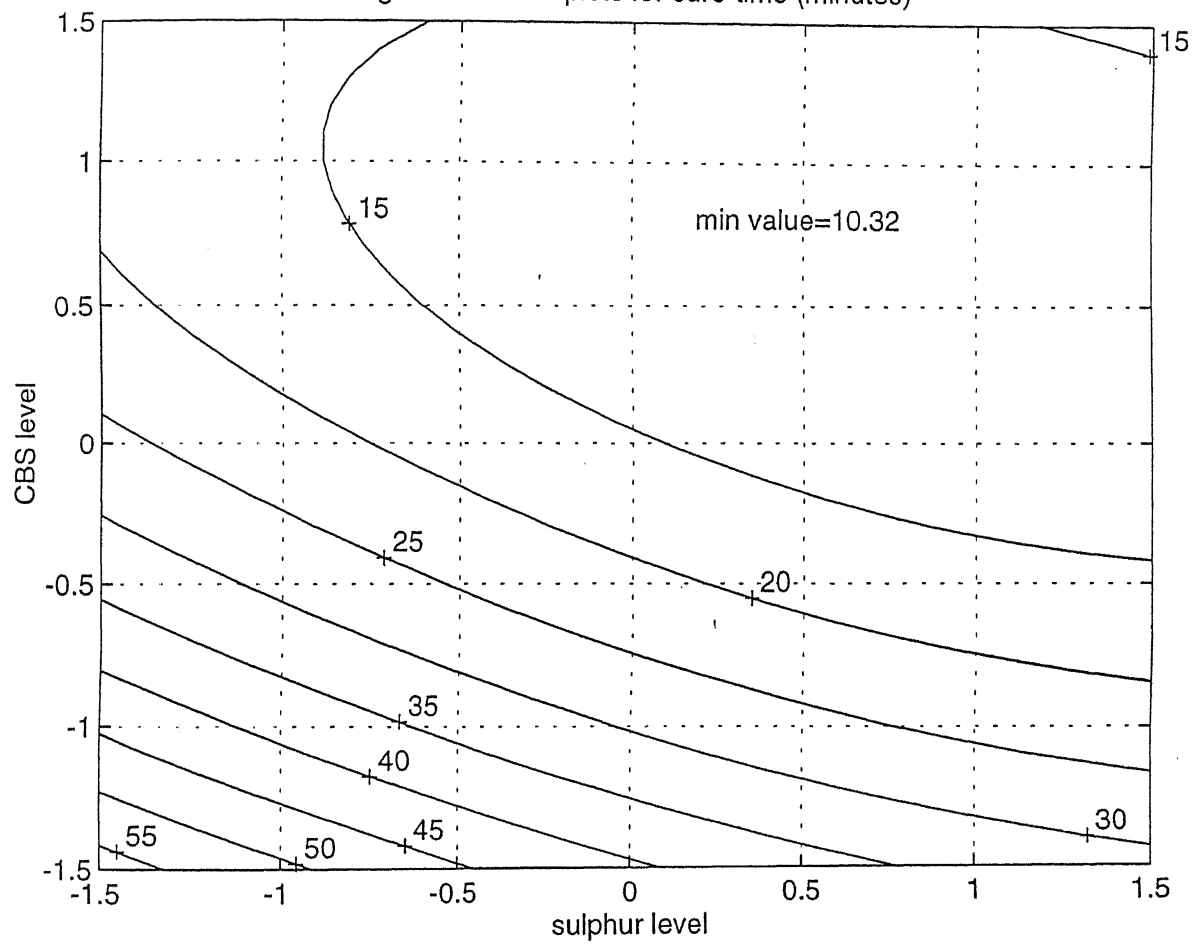


Fig.5.5: Response surface for cure-time

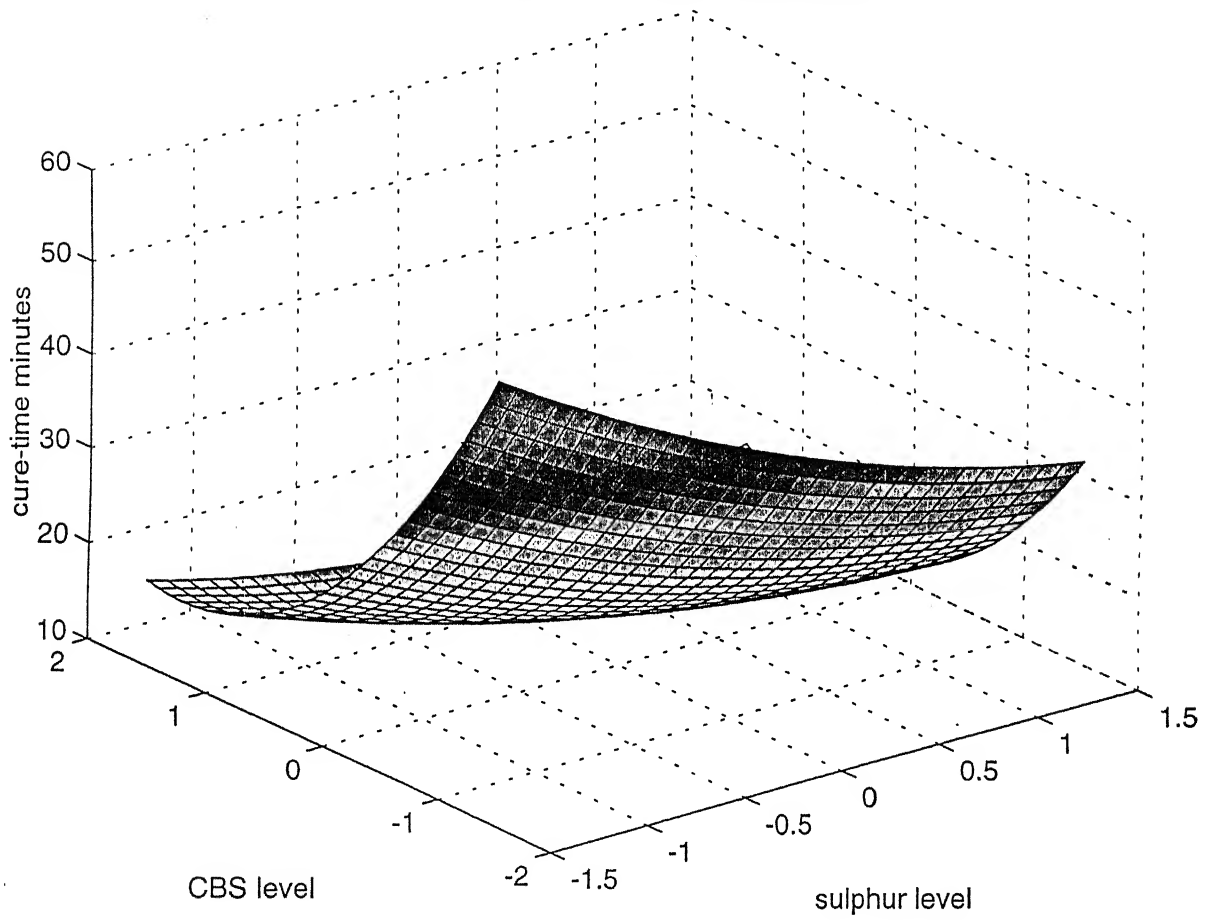


Fig.5.6: Contour plots for Modulus, M-100 (ksc)

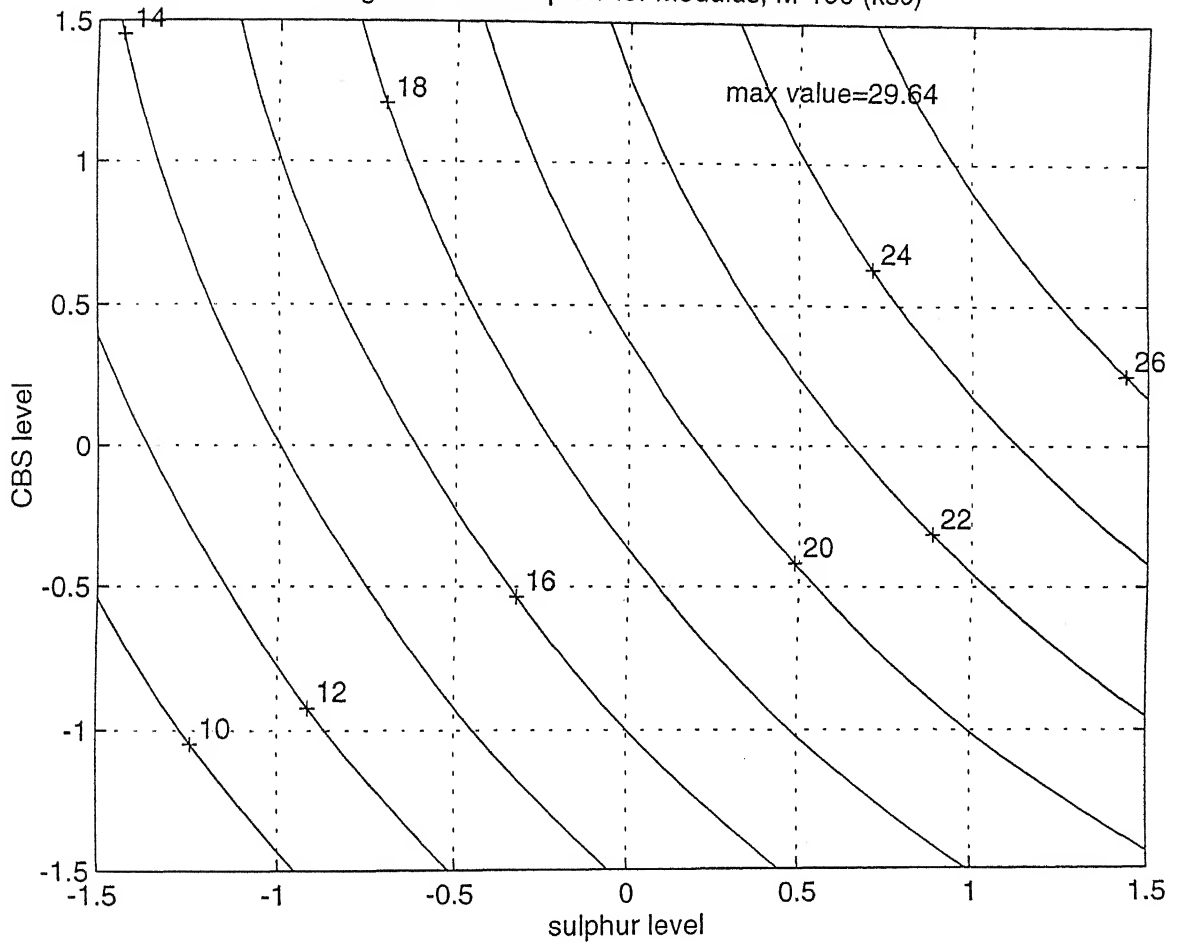


Fig.5.7: Response surface for Modulus, M-100

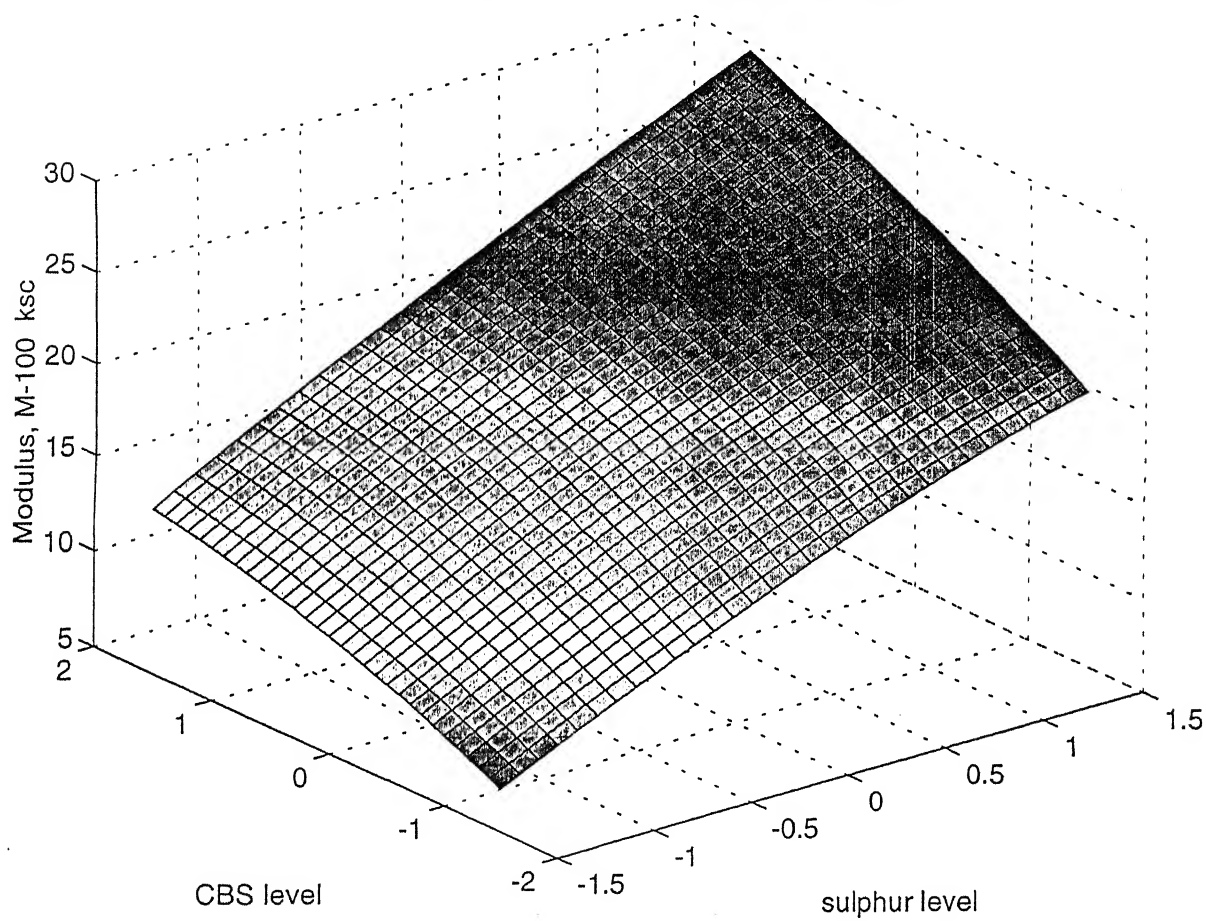


Fig.5.8: Contour plots for Stress at 300% elongation, M-300 (ksc)

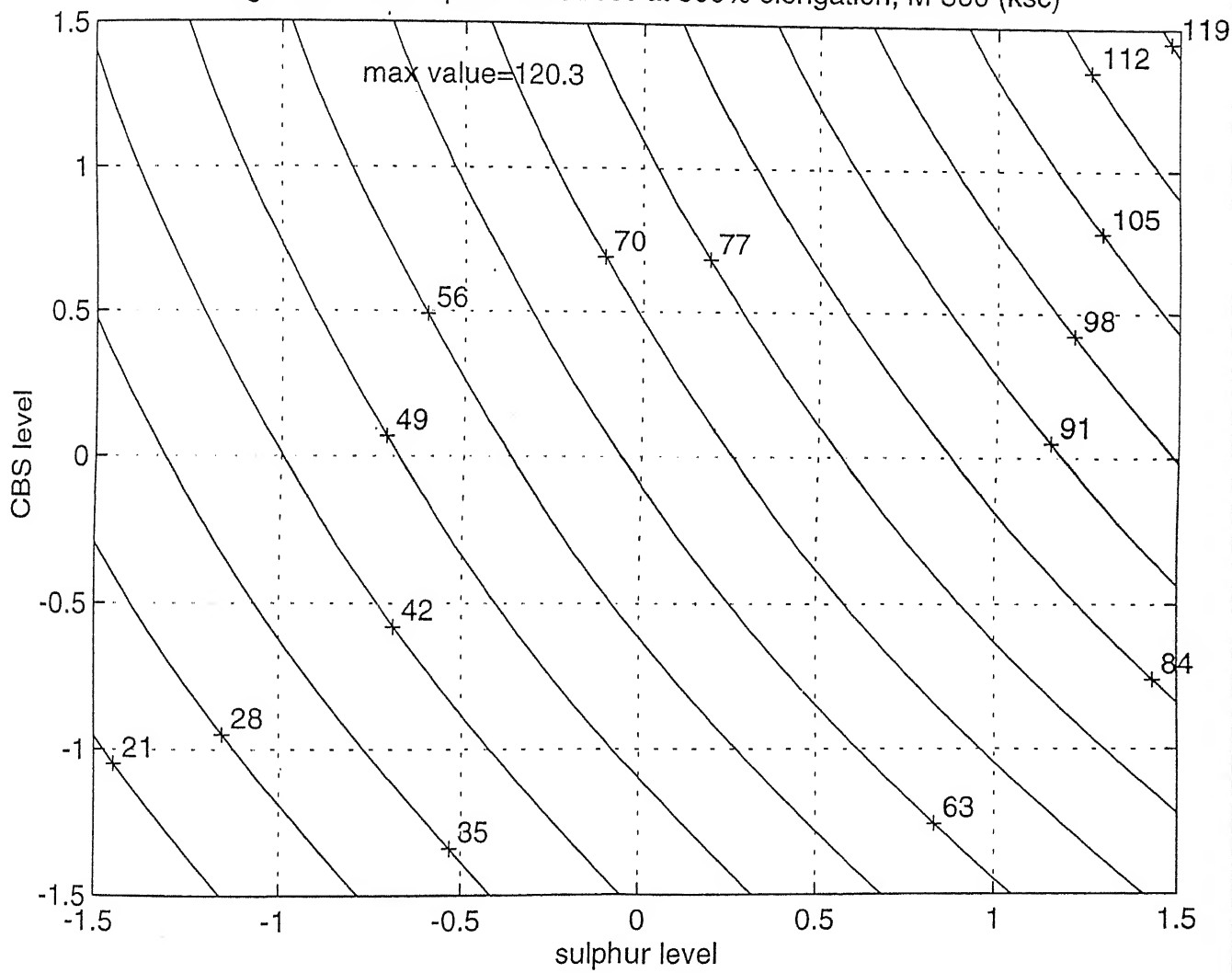


Fig.5.9: Response surface for Stress at 300% elongation, M-300

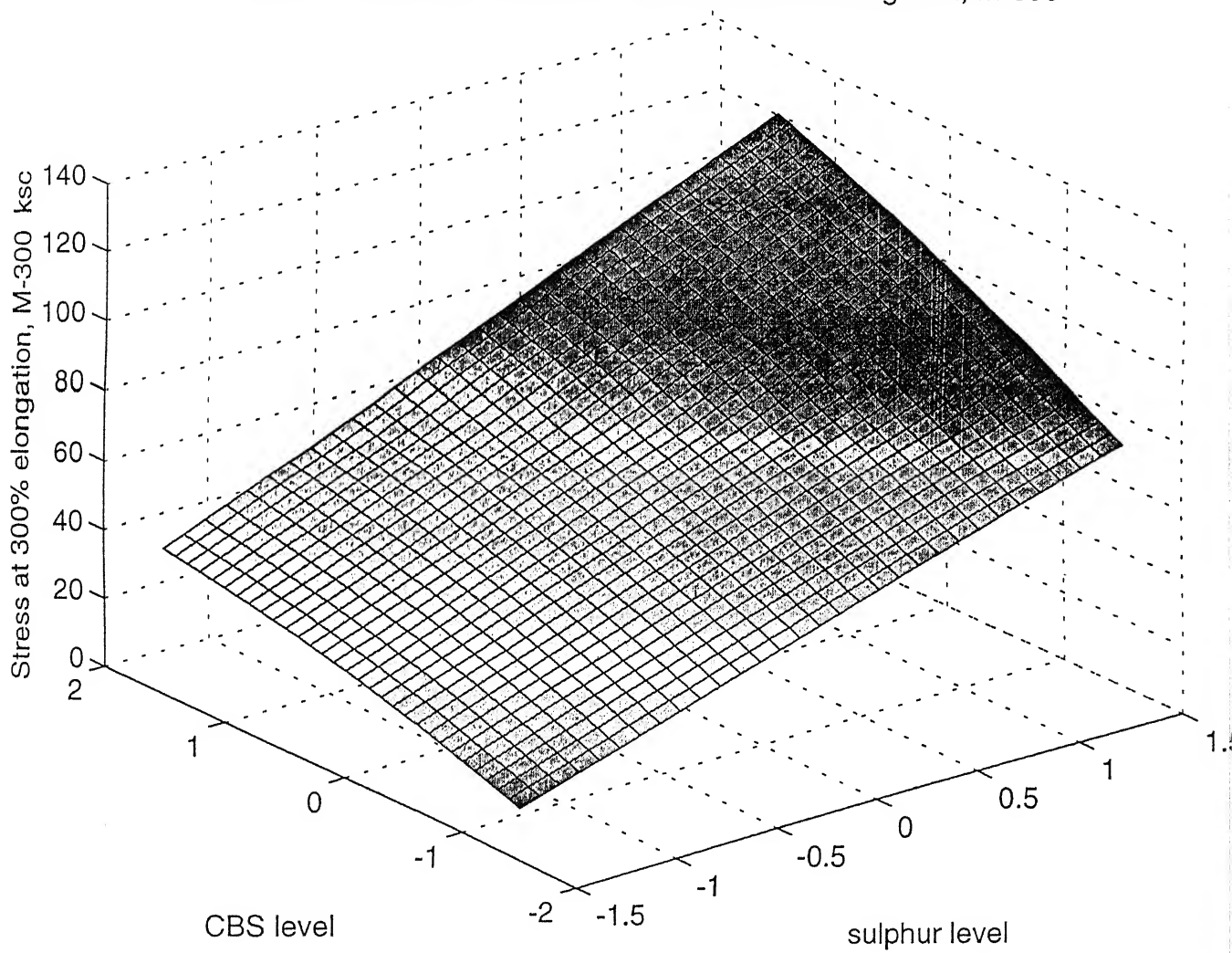


Fig.5.10: Contour plots for Hardness (Shore A)

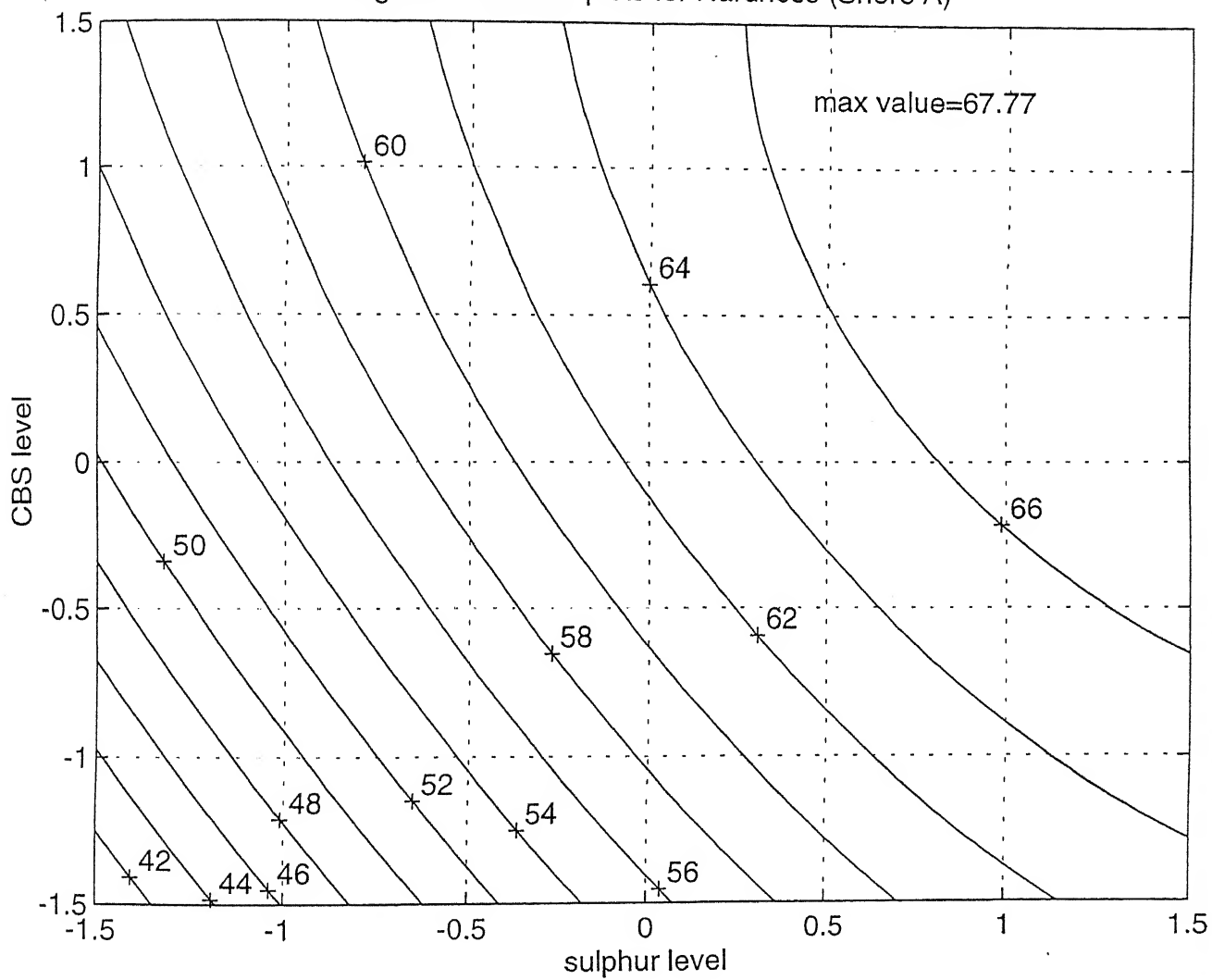
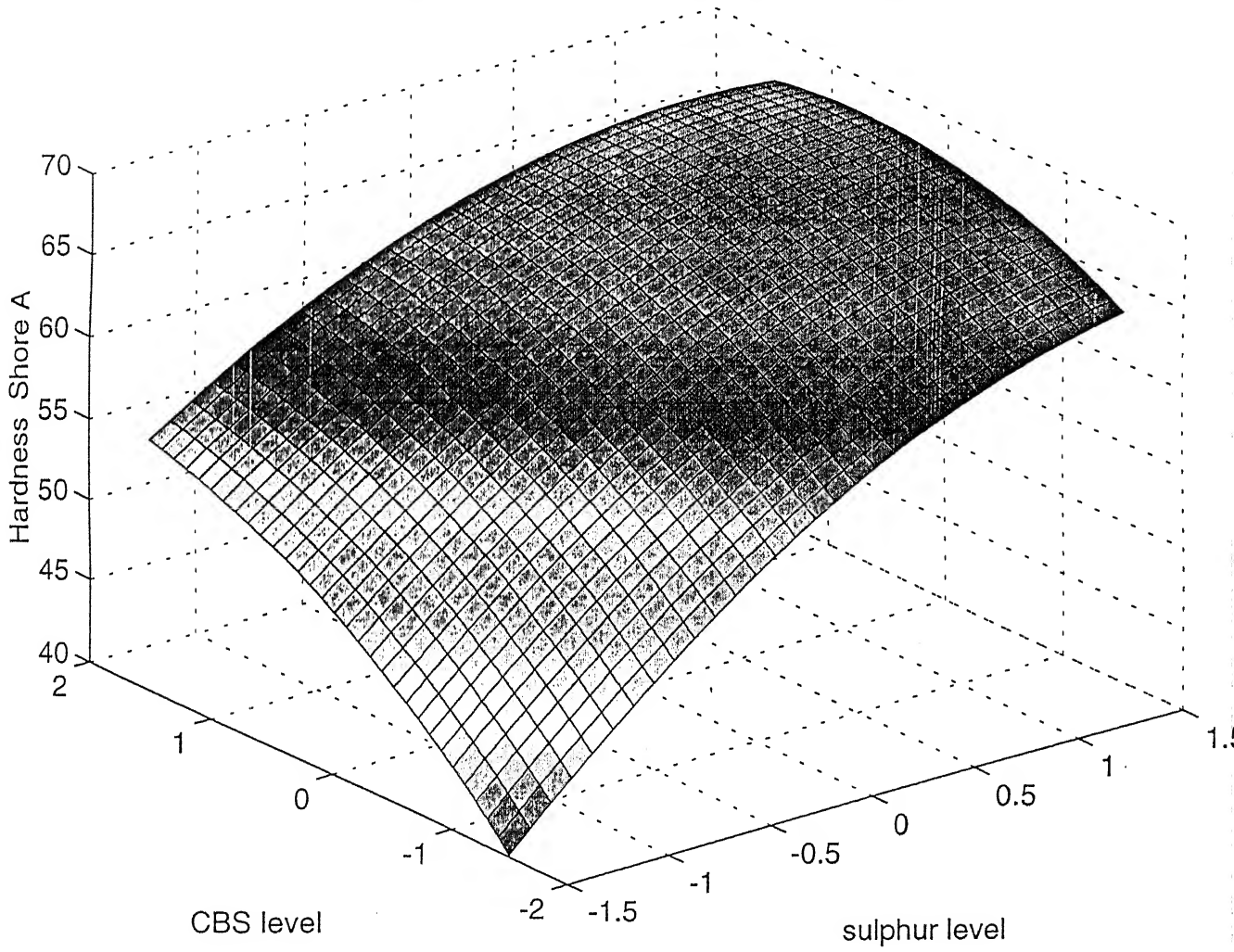


Fig.5.11: Response surface for Hardness



In case of **cure-time** contours (Fig. 5.4) we observe the following facts:

Low levels of curator (sulfur) and accelerator (CBS) lead to lower rate of reaction and a higher cure time. The torque values are low for such compositions due to low degree of crosslinking. The contours show decreasing trend of cure-time with increasing levels of sulfur and CBS, and approach a minimum of around 11 seconds in the region $S=0.5-1.0$ and $CBS = 0.5-1.0$ and then again start increasing very slowly. This phenomena is observed probably due to the fact that some of the poly-sulfide links formed initially breakup to give mono- and di-sulfidic links when level of sulfur is kept constant and that of CBS is raised progressively.

5.7.2 Mechanical properties

Modulus and Hardness (Figures 5.6 to 5.11)

As expected the values of M-100 and M-300 keep increasing consistently with the increase in levels of sulfur and CBS, thus leading to higher crosslink density. The larger the number of individual macromolecules bound together by the crosslinks, the larger the force required to produce a given deformation.

A similar reasoning is applicable to the consistent increase in hardness. As the degree of crosslinking rises, the hardness progressively increases until the material becomes ebonite. The more compact the network, the shorter the molecular segments between the crosslinks, hence tighter the network, which causes the requirement of more force to be applied to produce a constant deformation on the rubber surface. Thus the hardness values show an increasing trend.

Fig.5.12: Contour plots for Tensile strength (ksc)

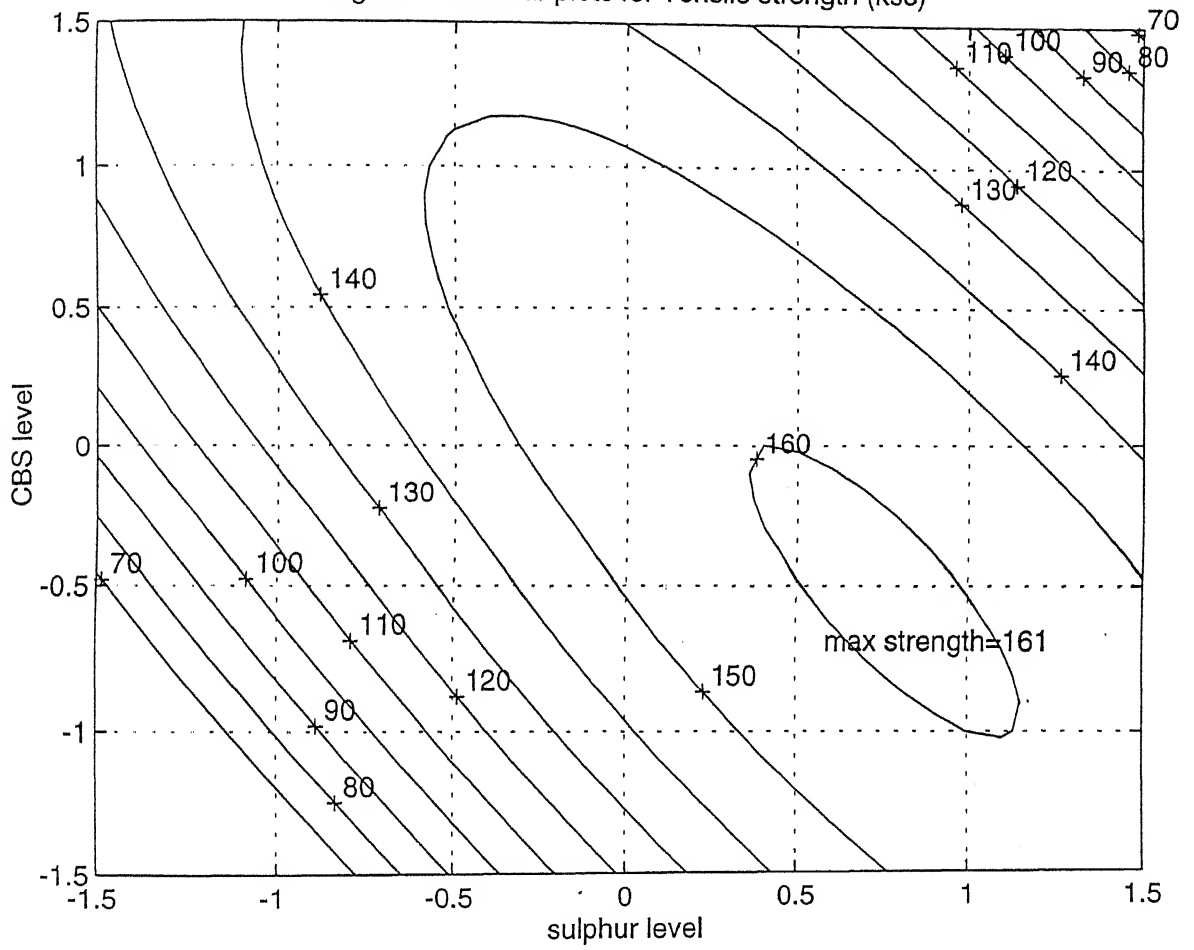


Fig.5.13: Response surface for Tensile strength

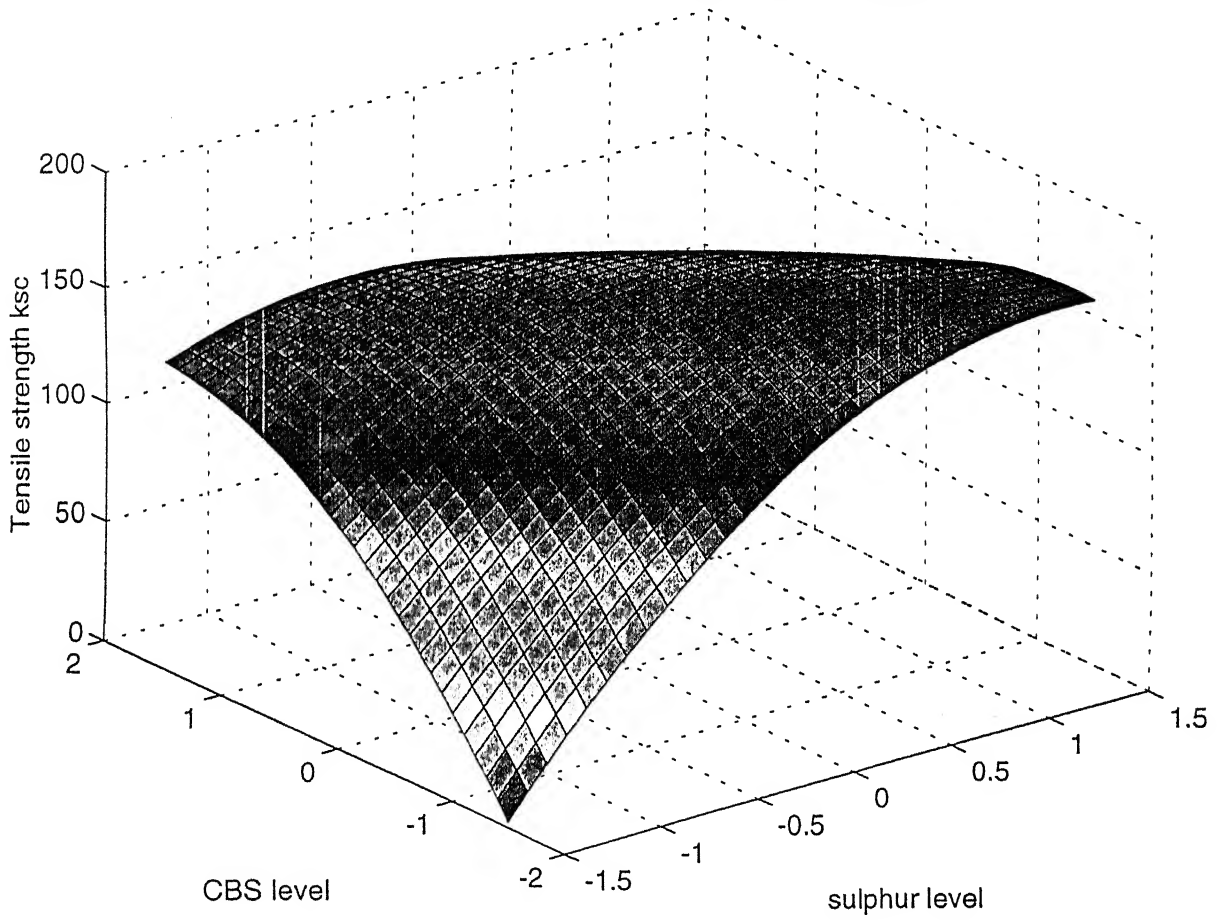


Fig.5.14: Contour plots for Elongation at break (%)

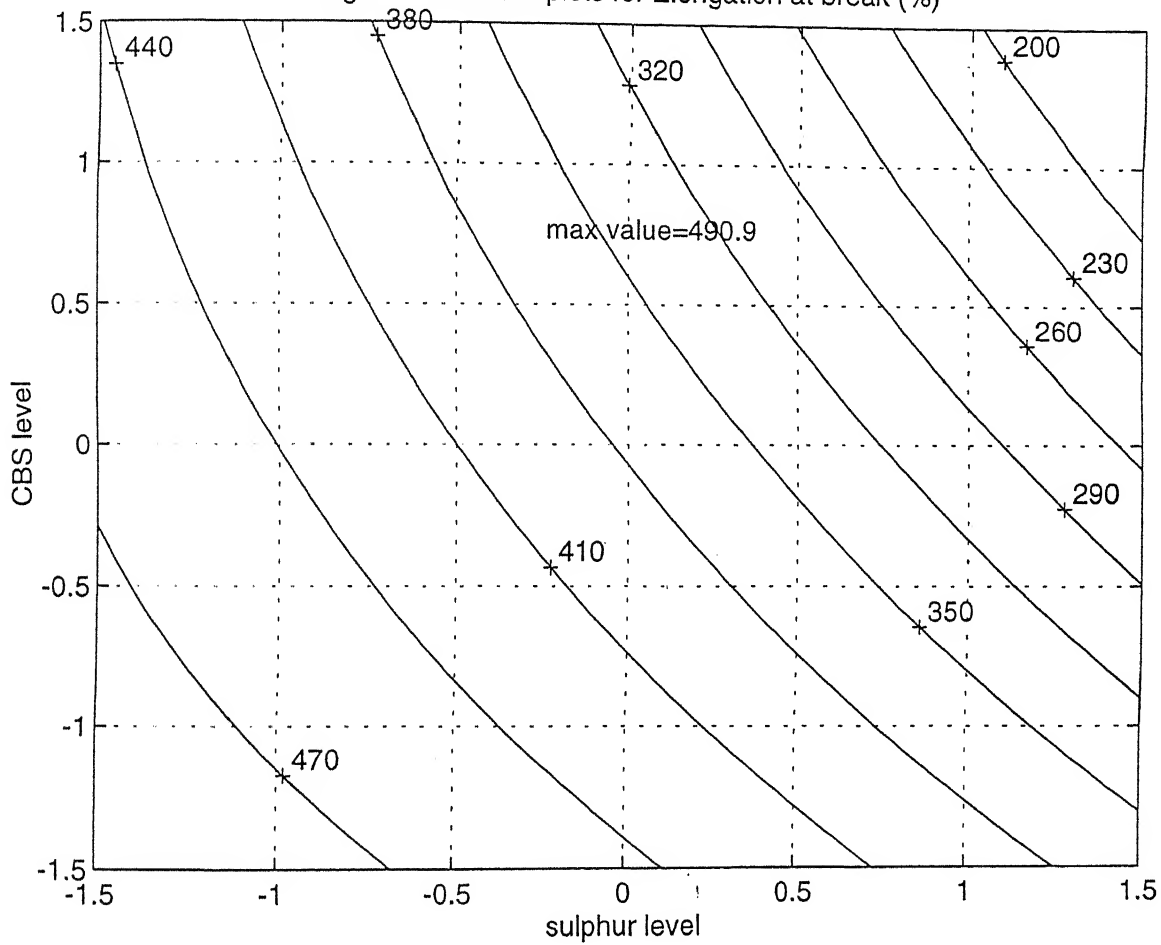


Fig.5.15: Response surface for Elongation at break

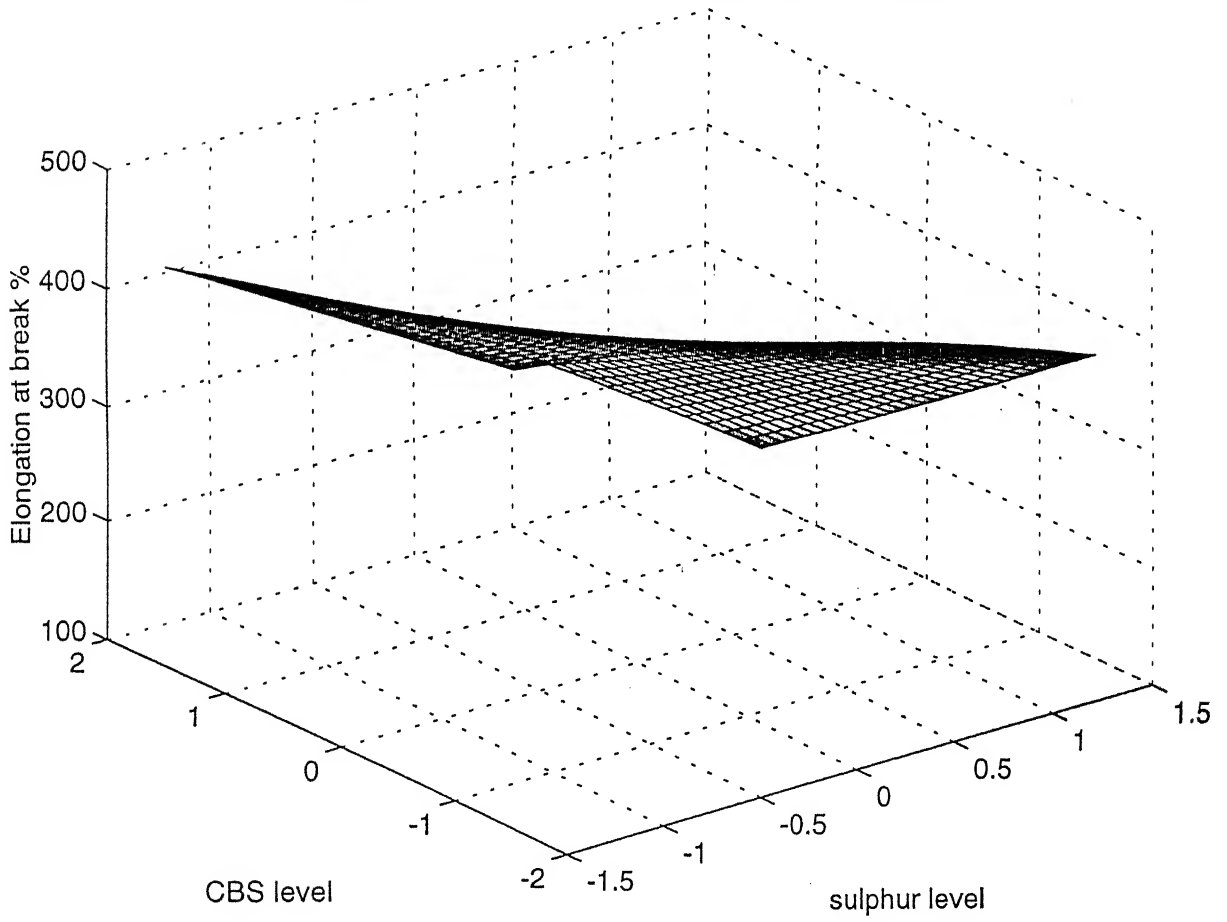


Fig.5.16: Contour plots for Compression set 24hrs/70 deg C (%)

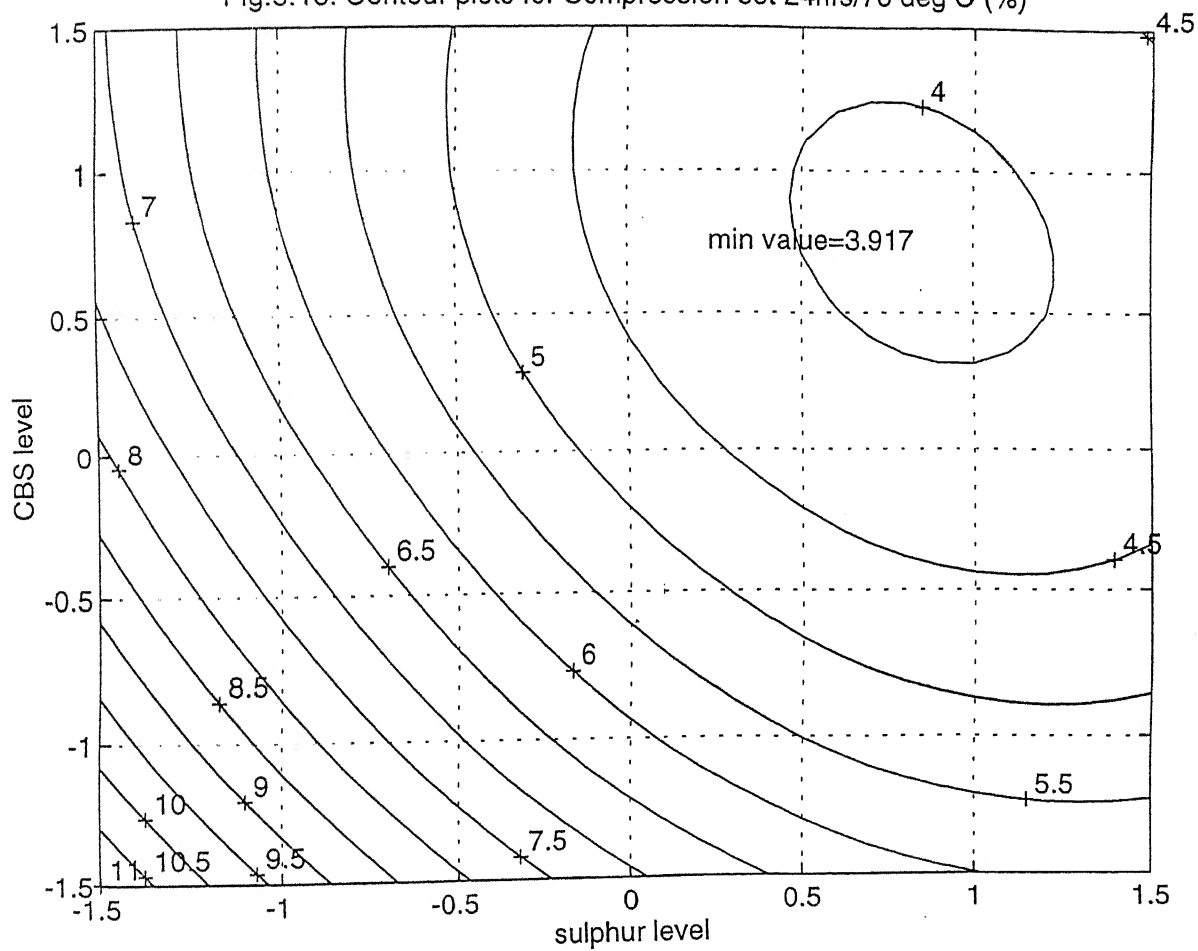


Fig.5.17: Response surface for Compression set 24hrs/70 deg C

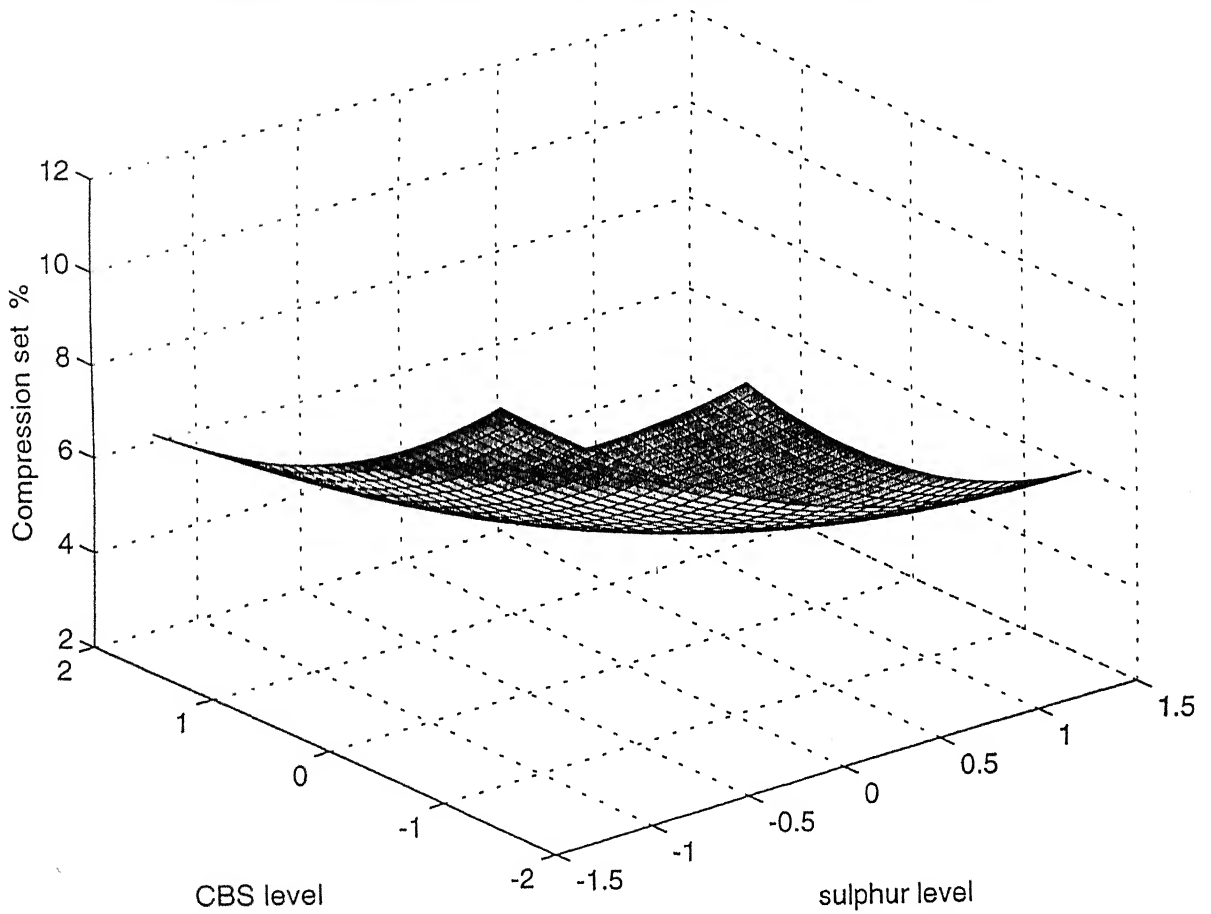


Fig.5.18: Contour plots for Compression set 72hrs/70 deg C (%)

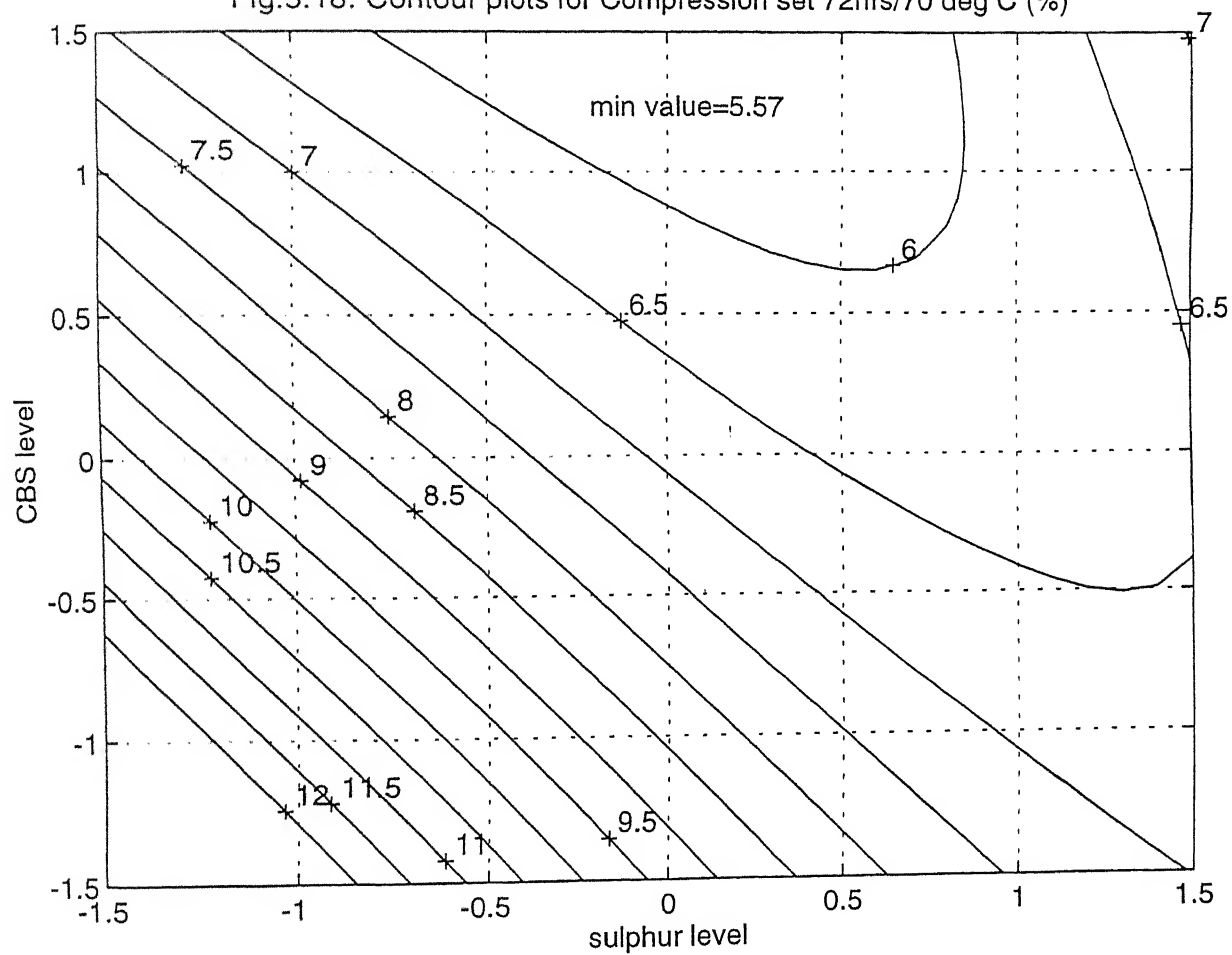


Fig.5.19: Response surface for Compression set 72hrs/70 deg C

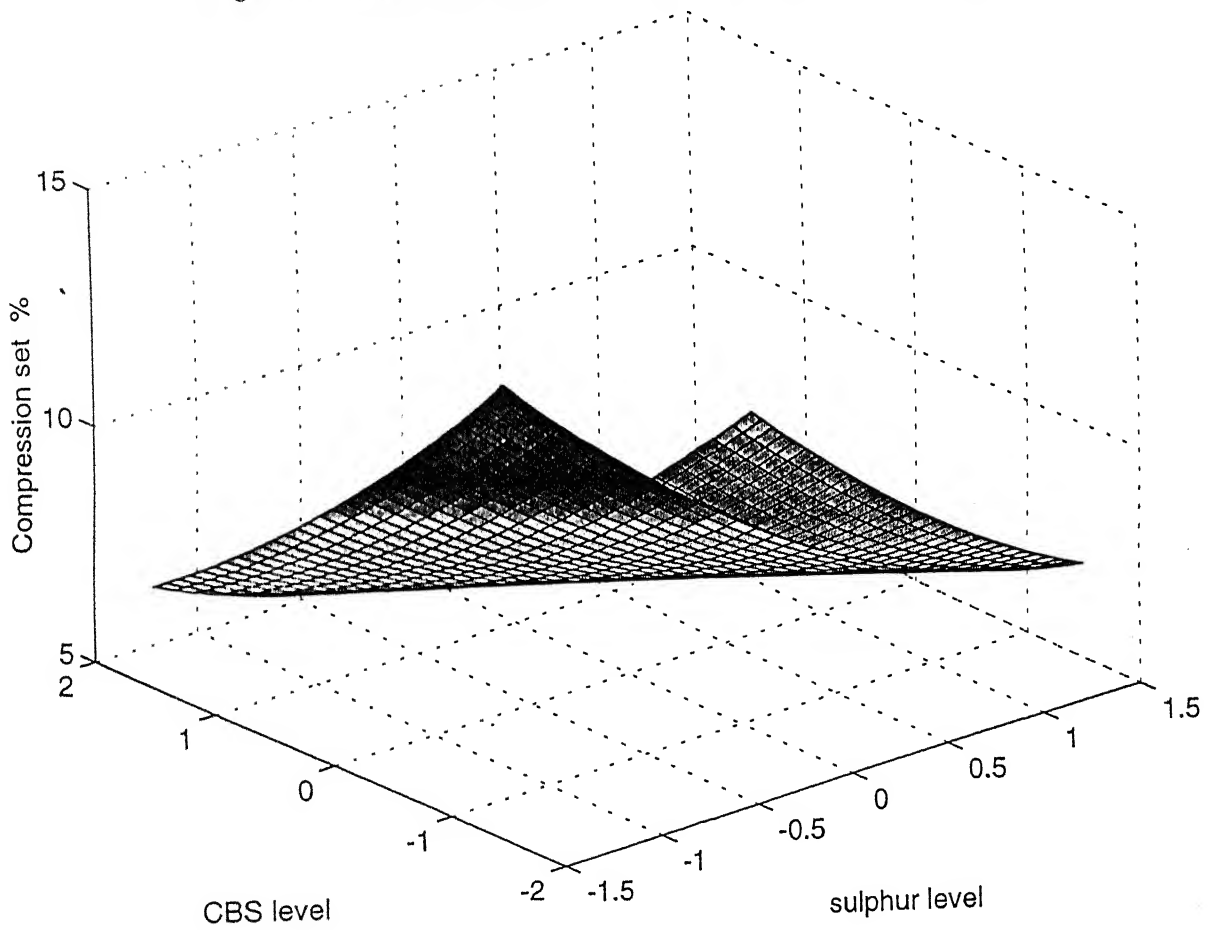


Fig.5.20: Contour plots for Tear strength (kgf/cm)

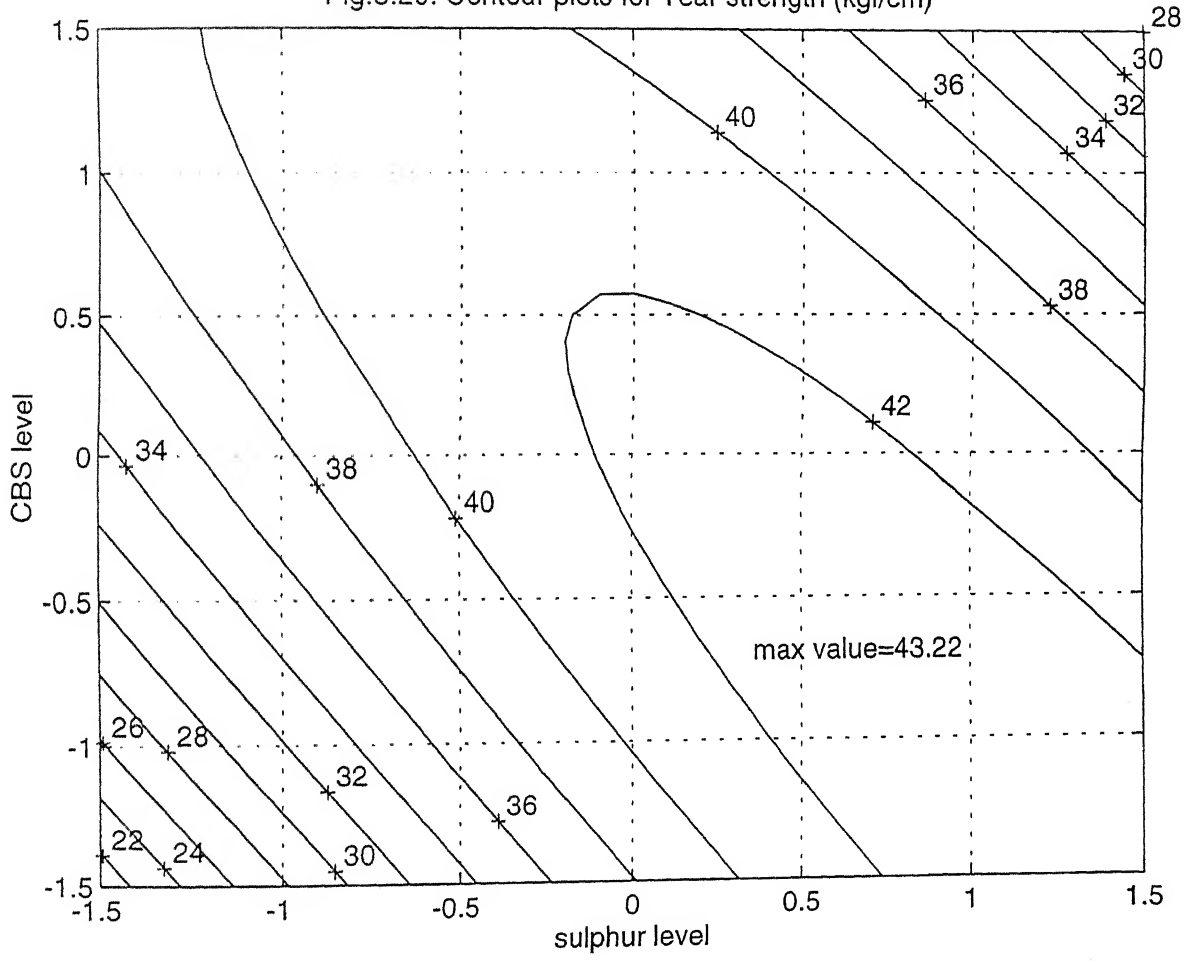
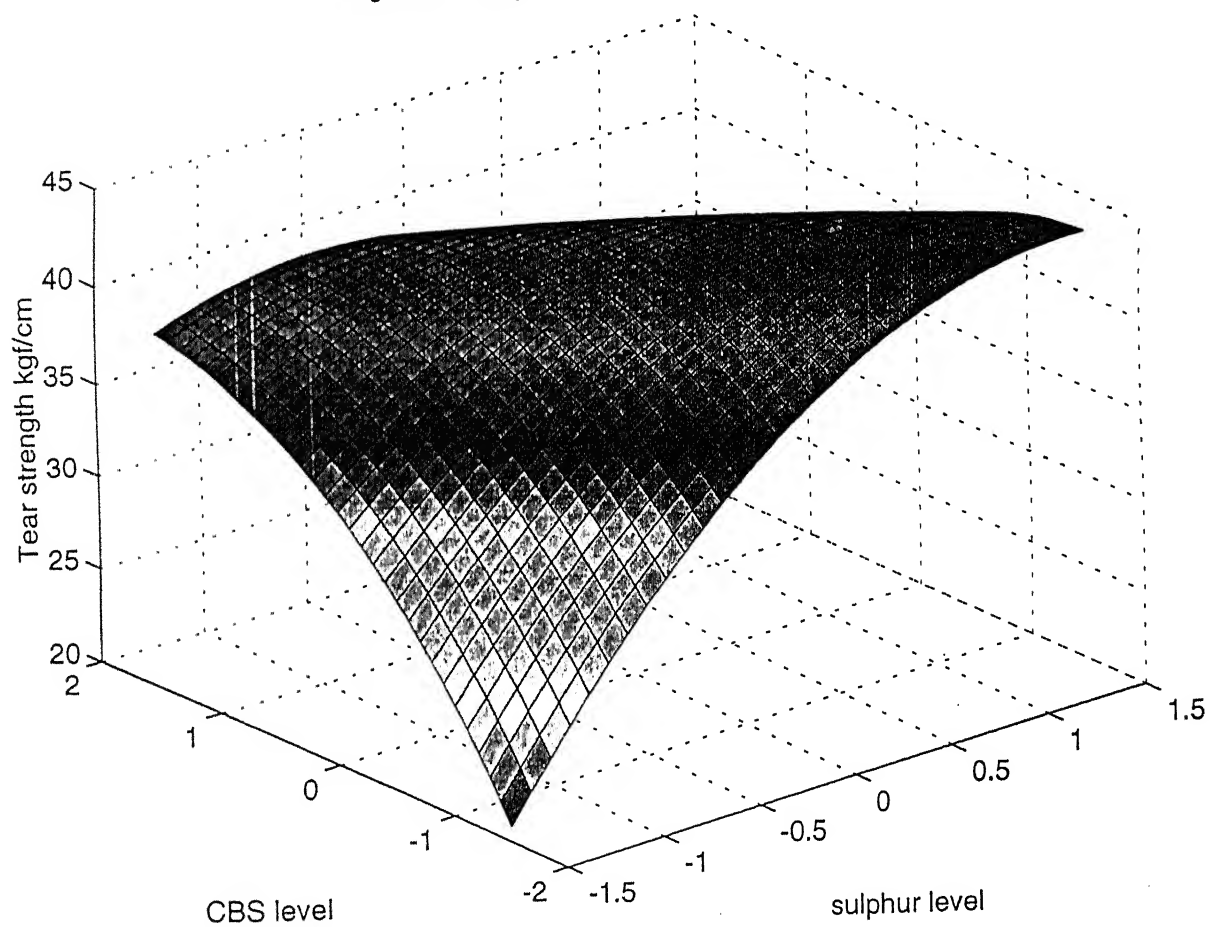


Fig.5.21: Response surface for Tear strength



Tensile strength (Figures 5.12 and 5.13)

Unlike modulus, the tensile strength does not rise continuously with the increase in sulfur and CBS levels. Instead, it increases initially, then decreases as the crosslink density is increased beyond an optimum level. In the present study the maximum in tensile strength is observed in the region around the point $S=0.75$ and $CBS=-0.5$. At a given degree of crosslinking the tensile strength is highest in vulcanizates with polysulfide bonds; it rises as the quantity x increases in $C-S_x-C$ crosslinks. This is why the increase in tensile strength is more pronounced when sulfur level is increased. In case of Styrene-butadiene rubber which does crystallize on deformation, the fall in tensile strength with further increase in sulfur level can be explained as follows. When overcrosslinking takes place which is irregular, the network may easily be overstrained, with the result that individual chains are no longer able to withstand the load and the material fails.

In case of natural rubber also a similar trend is noticed. Presumably a part is played here by crystallization due to the orientation of the molecular chains. The crystallites initially serve, both as filler particles and crosslinks, holding the material together in much the same way as chain entanglements do. However, fairly large additions of sulfur, which get built in intramolecularly, deprive the rubber of its capacity for orientation and hence of its ability to become tougher when elongated, thus leading to reduction in tensile strength.

Elongation at break (Figures 5.14 to 5.15)

The elongation at break decreases with increasing degree of crosslinking or in other words with the increasing levels of sulfur and CBS.

Compression set (Figures 5.16 and 5.17)

Compression set is improved with increase in crosslink density. It is also a function of types of crosslink. Monosulfidic crosslinks give lower compression set values than the poly-sulfidic crosslinks. Efficient vulcanization systems generally display lower set values, especially at high temperatures of testing. This is reason why we obtain lower set values as we approach the upper right regions of the compression set contours.

Tear resistance (Figure 5.20 and 5.21)

In tearing process, chains must be broken. the surfaces of tear cracks are rough on a molecular scale since the tear follows a path of least resistance to minimize the number of chains that are broken. The first chains to be broken are those in a taut configuration; as the tearing proceeds, other chains become taut and break.

In our case the contours show a similar trend as that with the tensile strength. It is known that the tear resistance increases to a maximum as the crosslinking of rubber increases, and then the tear resistance rapidly decreases with higher degrees of crosslinking. The best degree of crosslinking for tear resistance is that which produces the highest tensile strength of the rubber. This is the degree of crosslinking that requires the highest energy to break the rubber.

5.8 LOCATING OPTIMUM RESPONSES (OPTIMIZATION)

When a polynomial representation of a response surface is obtained, the experimenter is interested in determining the factor levels that provide an optimum response. The preferred approach for accomplishing this task is by contour plotting method. This use of contour plots is preferred for a variety of reasons. The foremost of these is that in

most practical situations there is more than one response of interest in an experimental program. Thus, identification of an optimum in any one response is not as important as is knowing the tradeoffs available among several responses. Whether there is a set of predictor-variable conditions that will result in the optimum of all responses simultaneously becomes apparent when contours are overlaid.

A second reason for employing this graphical method is that in addition to the optimum conditions being apparent in a contour plot, there may also be portions of the experimental regions where the response is insensitive to changes in the predictor-variables. Where a response is robust to changes in predictor-variable values is important, especially in designing for product quality.

A drawback of the contour-plot approach is that as the number of responses and particularly the number of predictor-variables increase, the number of plots to review may be very large. This can be minimized by eliminating nonsignificant variables from the model and putting predictor-variables involved in interactions and curvature on the two axes available while holding other predictor-variables at constant values. A contour plot is generated for each response at each combination of the levels of the predictor variables that are being held fixed. a rule of thumb that keeps the number of plots within bounds while making it large enough to allow the salient features of the system under study to be seen is to have each predictor variable being held constant take on three equally spaced values.

The question of optimum response can be mathematically investigated. If a maximum or minimum response value exists, it corresponds to the predictor-variable values that are a solution of the set of equations obtained by setting each of the partial derivatives of the estimated response function with respect to the predictor-variables equal to

zero. The predictor-variable values that satisfy this set of equations are called a stationary point (in a k dimensional space). Canonical analysis is a mathematical approach that can be used to determine the stationary point and whether it represents a maximum, minimum, or saddle point.

From the contours plots in figures 5.2 to 5.20, we can draw the following inferences in the designed experimental region.

1. The degree of crosslinking keeps increasing with the increase in the levels of sulfur and accelerator. This is evident from the rheometer maximum torque contours.
2. The cure time of any compound cannot be lower than around 11 minutes whereas it can vary upto 55 minutes.
3. The modulus values vary as given

M-100 : 10-29 ksc (kgf/cm²)

M-300 : 21-120 ksc

4. The maximum hardness attainable with this set of variables is 68 shore A.
5. The maximum tensile strength possible is 161 ksc whereas elongation at break varies between 200-491%.
6. Similarly the minimum compression set values at 70°C possible are

24 hr at 70°C ~ 3.9%

72 hr at 70°C ~ 5.6%

7. The tear strength values vary between 30-43 kg/cm.

Our aim is to check by this method if a compound can be formulated which can simultaneously meet the following mechanical and cure properties.

Cure time	< 15 minutes at 145°C
Tensile strength	≅ 150 ksc

Tear strength	$\cong 42 \text{ kgf/cm}$
Elongation	between 320 to 380%
Modulus M-100	$\cong 20 \text{ ksc}$
Stress at 300% elongation M-300	$\cong 70 \text{ ksc}$
Compression set 24hr/70°C	$\leq 4.5\%$
Compression set 72hr/70°C	$\leq 6.5\%$
Hardness	$\geq 64 \text{ shore A}$

By overlaying the contour plots for these responses we come across the coded combination of $S=0.5$ and $CBS = 0.0$, which would meet the desired properties. Thus the rubber formulation arrived at from this method would be as given in table 5.5:

Table 5.5: Recipe for optimum responses

Ingredient	phr
Low styrene SBR	100.0
Carbon black (GPF)	70.0
Zinc oxide	3.0
Stearic acid	1.0
Naphthenic oil	14.0
Accinox TQ	1.0
Paraffin wax	0.5
Sulfur	2.00
CBS	2.10

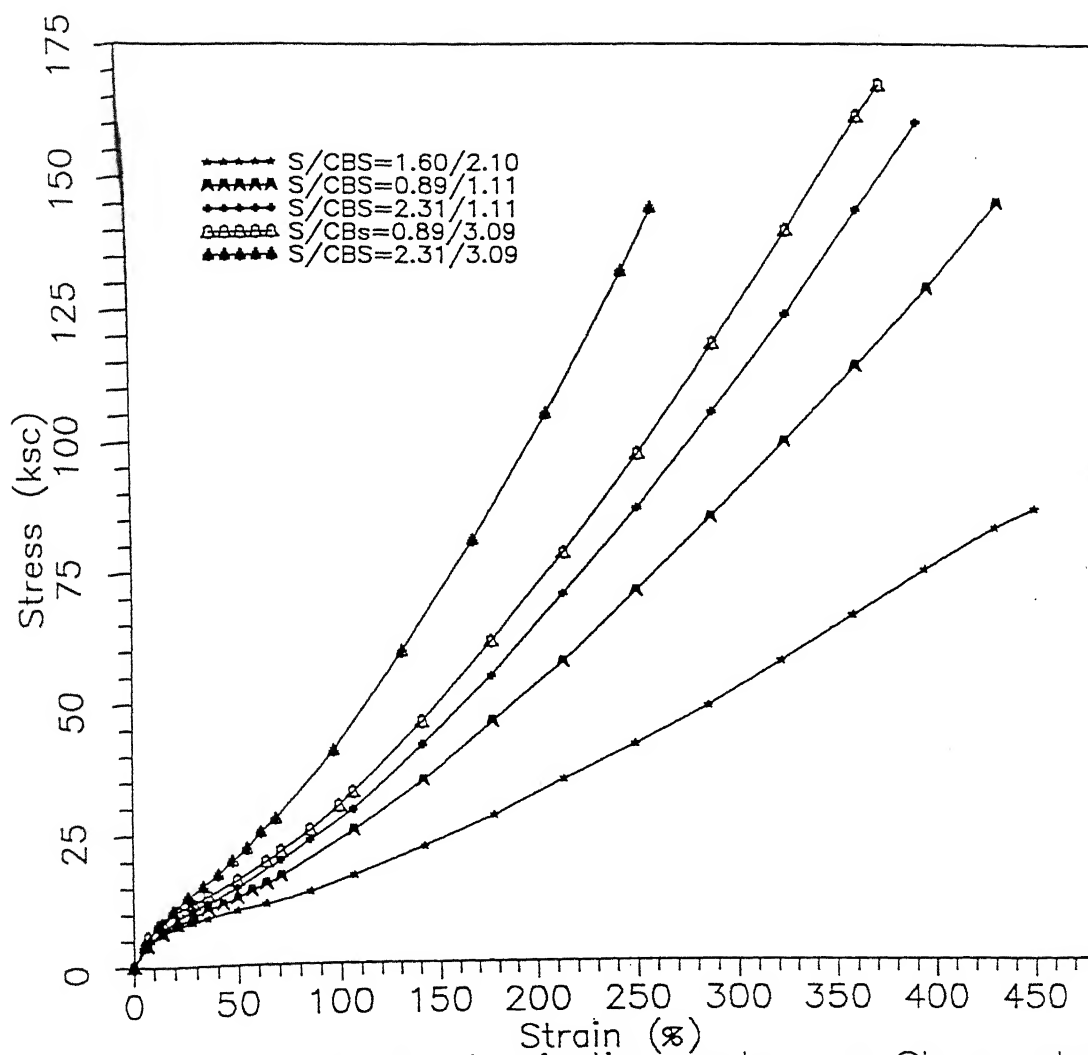


Fig.5.22: Effect of vulcanization system on Stress-strain characteristics

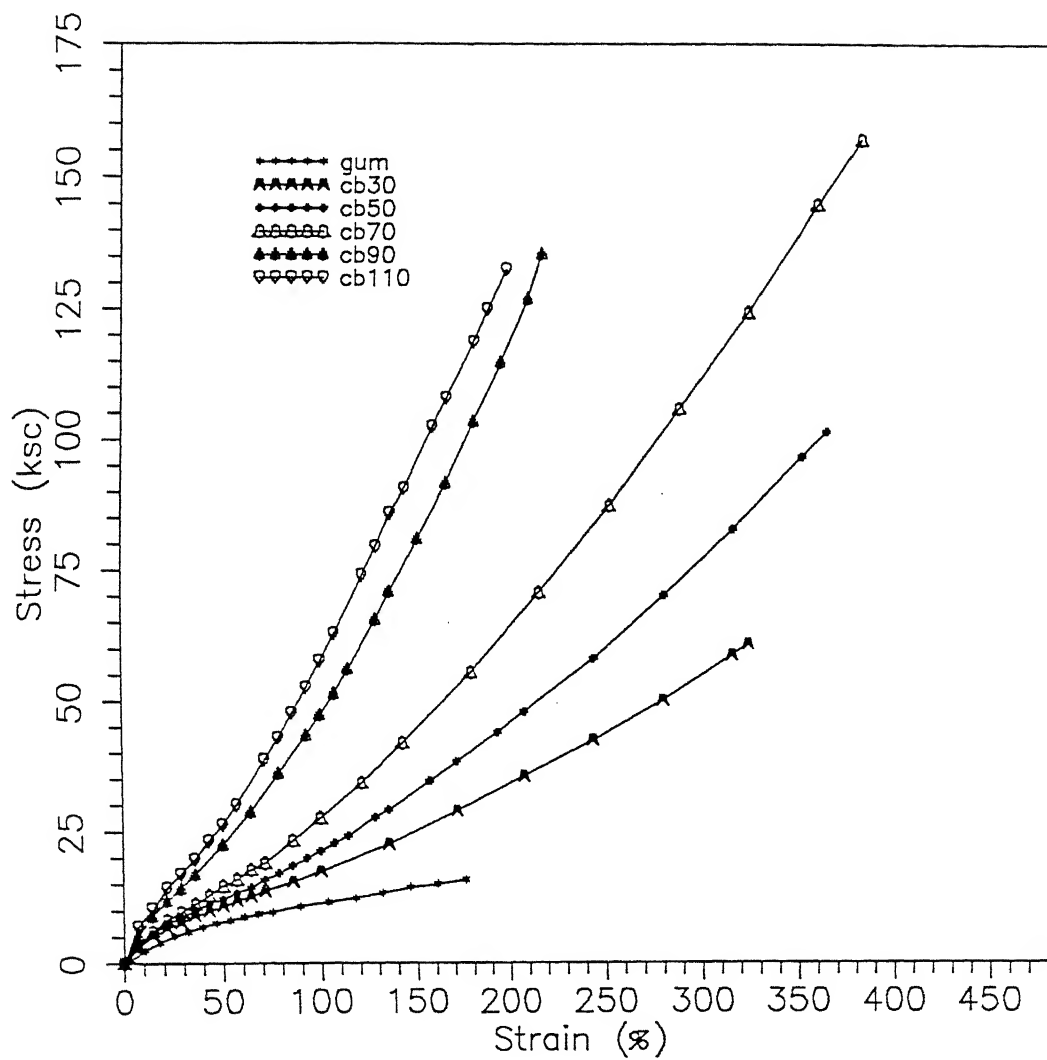


Fig.5.23: Effect of filler loading on stress-strain characteristics

5.9 STRESS-STRAIN CHARACTERISTICS OF CARBON BLACK FILLED LSBR VULCANIZATES

5.9.1 Effect of vulcanization system

As seen in figure 5.22 with the change in vulcanization system from conventional vulcanization (CV) to efficient vulcanization (EV) the slope of the curves decrease in the stress-strain plots. There is a fall in the modulus values of rubber. Similar trends were observed in the contour plots (figures 5.6 and 5.8) also. This is because the degree of crosslinking increases with increase in sulfur levels. The larger the number of individual macromolecules bound together by the crosslinks in the course of vulcanization, the larger is the force required to produce a given deformation and the stiffer is the vulcanizate.

5.9.2 Effect of Filler loading

Addition of a reinforcing filler like Carbon black improves modulus, tensile strength and tear resistance as evident from table 5.5 and fig. 5.23. But this improvement of properties is, however, not continuous; when the weight percentage of filler increases further, the point at which there is insufficient rubber to bind the filler is eventually reached. A noticeable decrease in strength is visible after this point (carbon black level : 70 phr) as seen in table 5.6. Carbon black increases the tensile strength by allowing the applied load to be shared amongst a group of chains, thus decreasing the chance of a break to propagate. The recipe for rubber compounds from mixes F1 to F6 where the carbon-black filler and naphthenic oil levels were varied is given in table 5.7.

Table 5.6: Property variation with increase in filler loading

Mix No.	Filler loading phr	Tensile strength ksc	M-100 ksc	Elong -ation %	Tear strength kg/cm	Hardness Shore A
F6	0	15.8	11.3	176	10.1	40
F3	30	60.9	17.4	323	29.8	47-48
F1	50	101.3	21.3	363	36.1	52
F2	70	156.9	27.6	380	42.4	56-57
F4	90	135.3	47.3	214.3	40.1	64
F5	110	132.4	57.7	195.7	39.8	65-67

Table 5.7: Recipe for mix no. F1 to F6

Ingredient	phr					
Low styrene SBR	150.0					
Zinc oxide	4.5					
Stearic acid	1.5					
MBTS	1.0					
TMTD	0.5					
Sulfur	2.7					
Mix no.	F6	F3	F1	F2	F4	F5
Naphthenic oil	3.0	9.0	15.0	21.0	27.0	33.0
Carbon black	0	30	50	70	90	110

5.9.3 Effect of Temperature

Temperature has a great effect on all the stress-strain properties. At temperatures well above T_g , the modulus is high and the elongation to break (ϵ_B) is low. When increasing the temperature above T_g , the following behaviour is characteristic: the modulus decreases whereas the elongation at break (ϵ_B) increases. Finally, at high temperatures where the material is extremely soft, the modulus is too low and ϵ_B may again decrease. We have tested the rubber samples from s.no.5 as shown in table 5.2 at three different temperatures ($+50^\circ\text{C}$, $+20^\circ\text{C}$ and -50°C). The results are shown in figure 5.24.

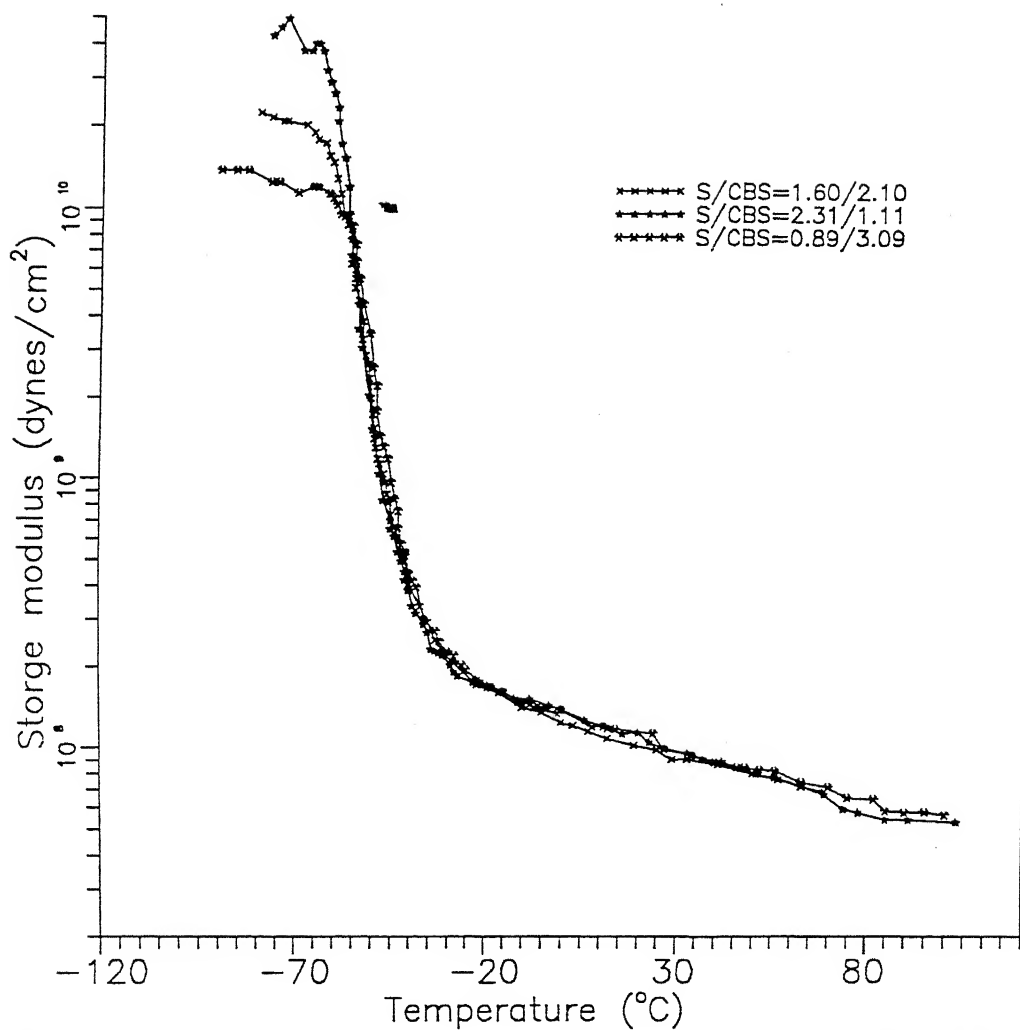


Fig.5.25: Dependence of storage modulus on temperature for carbon-black filled LSBR vulcanizates at different sulfur to accelerator ratios (Testing at 35 Hz.)

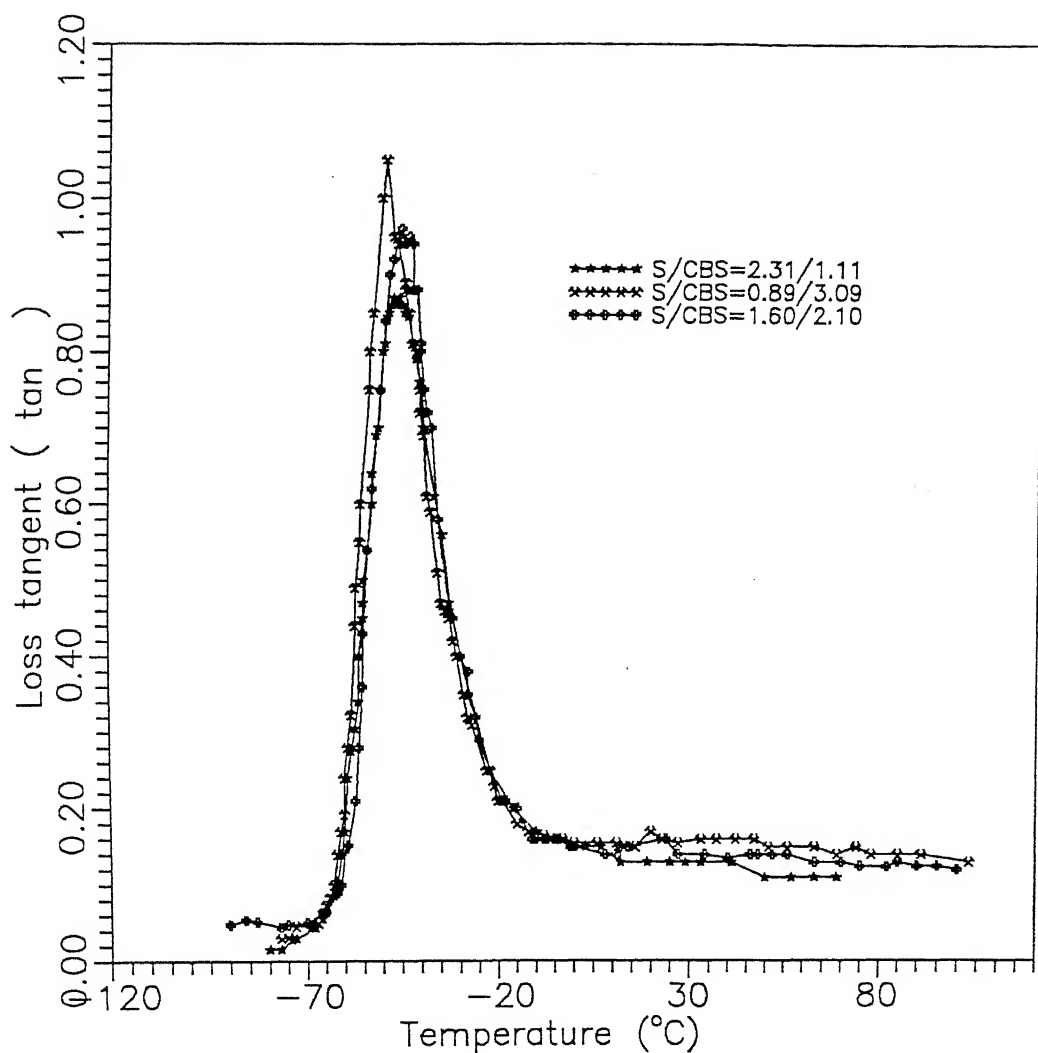


Fig.5.26: Dependence of loss tangent on temperature for carbon-black filled LSBR vulcanizates at different sulfur to accelerator ratios (Testing at 35 Hz.)

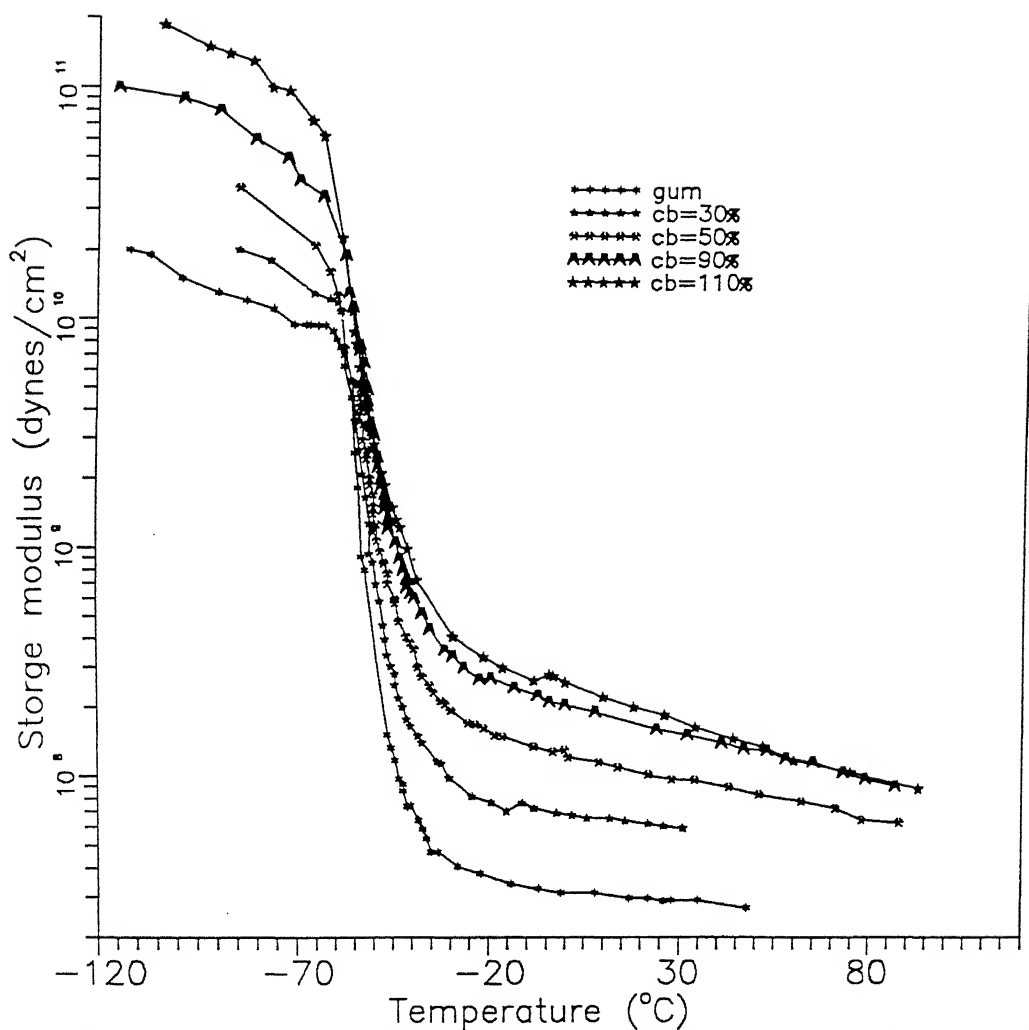


Fig.5.27: Dependence of storage modulus on temperature for carbon-black filled LSBR vulcanizates at different filler loadings (Testing at 35 Hz.)

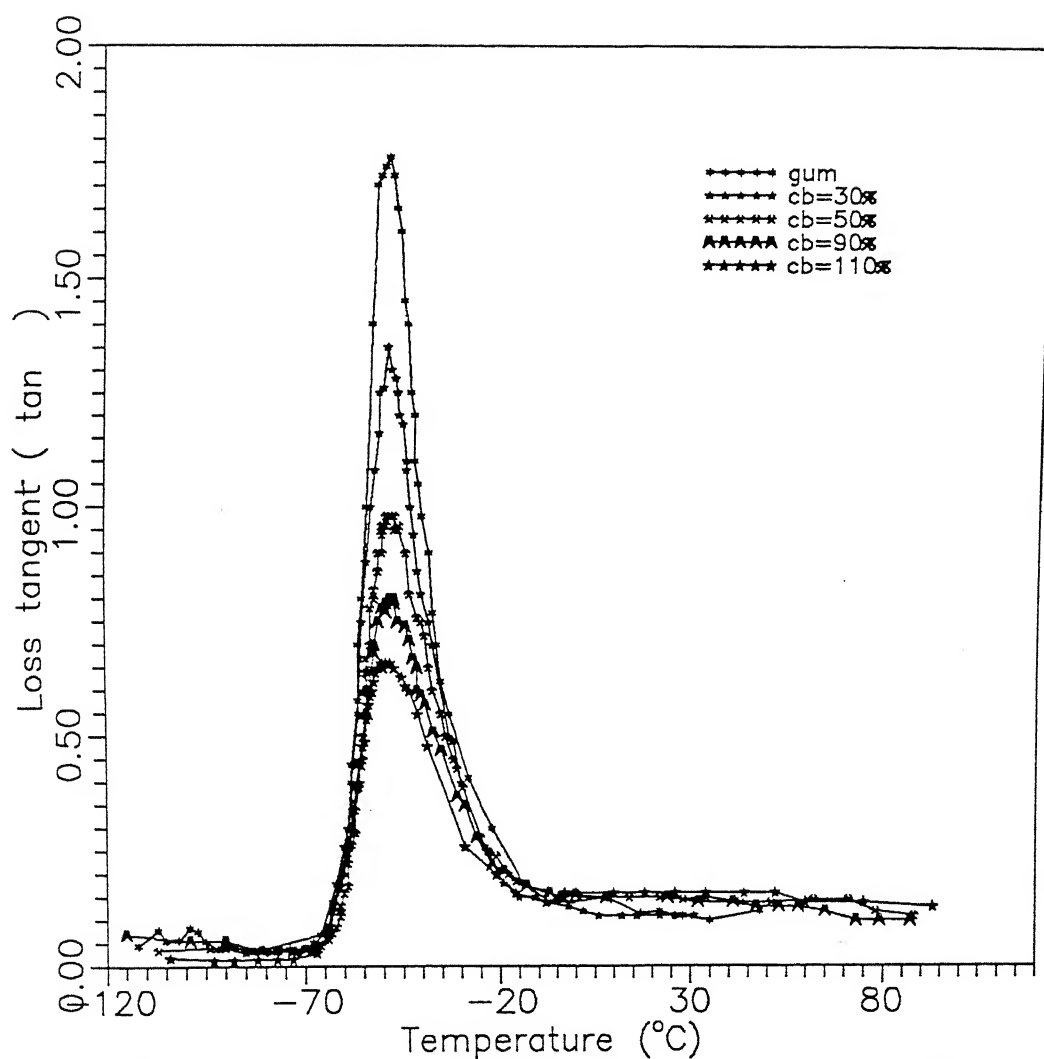


Fig.5.28: Dependence of loss tangent on temperature for carbon-black filled LSBR vulcanizates at different filler loadings (Testing at 35 Hz.)

5.10 DYNAMIC BEHAVIOUR AND DETERMINATION OF T_g

An attempt was made to study the change in dynamic behaviour of Low styrene-butadiene rubber vulcanizates by changing the vulcanization system and filler loading. The dependence of storage modulus and loss tangent on temperature are plotted in figures 5.25 to 5.28.

5.10.1 Effect of vulcanization system

The changes in dynamic behaviour of a polymer with degree of crosslinking are more pronounced in polymers which are rather highly crosslinked than normal rubbers. The effect of crosslinking on dynamic properties of vulcanized rubber is evident above T_g . The storage modulus of a crosslinked rubber does not decrease with increasing temperature in the plateau region as seen in figure 5.25. The loss tangent is a sensitive indicator of crosslinking. At temperatures well above T_g , the damping decreases with increasing degree of crosslinking. A plot of $\tan \delta$ as a function of temperature is shown in fig. 5.26. The effect of higher crosslinking is to slightly increase the temperature and decrease the height of loss peak.

5.10.2 Effect of Filler loading

The dependence of storage modulus and $\tan \delta$ on filler level are shown in figures 5.27 and 5.28 respectively. Fillers have a larger effect in raising the storage modulus above T_g than below it. Fillers also introduce a broadening or lower slope in the transition region. At any given temperature, the storage modulus is found to increase with increase in filler loading due to negligible or no deformation in the rigid filler particles

and immobilization of rubber matrix at the filler surface. There is a lowering of peak observed in $\tan \delta$ with increase in filler level for the same reason.

5.10.3 Determination of Glass transition temperature, T_g

The dynamic properties of LSBR, expressed in terms of storage modulus (E') and loss tangent ($\tan \delta$), determined over a wide range of temperature at 35 Hz. are shown in figures 5.25 to 5.28. E' undergoes a large decrease around -49°C corresponding to the glass transition temperature (T_g). Loss tangent ($\tan \delta$) exhibits a peak value at T_g . This is because the damping is high in the glass-rubber transition region owing to the initiation of micro-Brownian motion [Murayama,1978]. Some of the molecular chain segments are free to move, while others are not. A frozen-in segment can store much more energy for a given deformation than can a free-to-move rubbery segment. Thus, every time a stressed, frozen-in segment becomes free to move, its excess energy is dissipated as heat.

CHAPTER 6

SUMMARY AND RECOMMENDATIONS

An attempt has been made to develop a Low Styrene-butadiene rubber compound suitable for use at low temperatures. The moulded products from this compound would be preferably used as O-rings, gaskets, dust seals, hermetic seals and vibration isolators in different stages of the Geo-stationary launch vehicle (GSLV) of the Indian Space Research Organisation (ISRO). Predictor -variables most affecting the properties of the compound were identified and a suitable design of experiments was selected to begin the study so as to yield the maximum possible information with minimum number of compounding trials.

In the beginning a few compounding trials were made to fix the filler (carbon black) loading level at 70 phr.

After conducting the compounding trials as per the design of experiments the required mechanical and other properties were evaluated. Models were generated for these responses of interest by linear regression analysis using MATLAB (version 4.2) software.

The optimum levels of other predictor-variables viz. sulfur and CBS were determined making use of Response surface methodology. A combination of sulfur = 2.0 phr and CBS = 2.10 phr with other variables at levels fixed as shown in table 5.4 is found to meet the desired mechanical properties.

The glass transition temperature T_g for these compounds was determined and the effect of variation in the degree of crosslinking and filler loading on mechanical properties and dynamic behaviour of LSBR compounds was investigated.

FUTURE WORK

1. Similar work using Response surface methodology would be conducted on EPDM (Ethylene-propylene rubber) to study their suitability for use at low temperatures.
2. Besides the major components, oxidizer, fuel and binder; solid propellants contain a number of additives such as curatives, processing aids, burn-rate modifiers, antioxidants, etc. To achieve desired properties (viz. mechanical - tensile strength, modulus, elongation; ballistic - burn rate, maximum pressure etc.; and rheological) a number of experiments are conducted by varying the levels of the different ingredients in a trial and error method based on previous experience. However, no statistical techniques have been applied in designing propellant compositions in a systematic manner. It is proposed to arrive at optimized formulations in HTPB (Hydroxyl-terminated Polybutadiene) propellants using response surface methodology for PSLV and GSLV missions. HTPB is used as a binder in solid propellants.
3. RSM can also be applied to maximizing the yield of Hydroxyl-terminated Polybutadiene by optimizing the four predictor-variables namely : polymerization temperature, concentration of the initiator, polymerization time and stirring rate in the polymerization of Butadiene.
4. Pyrocompositions used in pyrodevices like Igniters for solid rocket motors, electrically actuated devices (EEDs) and cartridge actuated devices (CADs) are mixtures of metallic fuel, oxidizers and minor other ingredients. These could be optimized for calorific value and other ballistic properties using Response Surface Methodology.

APPENDIX A

MODEL CALCULATION FOR CODED LEVELS

(EXPERIMENTAL DESIGN UNITS)

1. Determine the average of the two factor-level values. denote it by AVG.
2. Determine the midrange of the factor levels:

$$\text{MID} = (\text{upper level} - \text{lower level}) / 2$$

3. Code the factor levels :

$$\text{Coded level} = (\text{level} - \text{AVG}) / \text{MID}$$

For sulfur the upper level and the lower levels are fixed as 2.31 phr and 0.89 phr respectively. We want to determine the coded level for 2.60 phr

$$\text{AVG} = (2.31 + 0.89) / 2 = 1.60$$

$$\text{MID} = (2.31 - 0.89) / 2 = 0.71$$

$$\text{Coded level} = (2.60 - 1.60) / 0.71 = 1.414 \text{ edu}$$

APPENDIX B

MODEL CALCULATION FOR ANALYSIS OF VARIANCE (ANOVA)

DATA FOR SHORE-A HARDNESS MEASUREMENTS

S. no.	Hardness (shoreA) Y_u	Predicted values $Y(x_u)$	Residuals $Y_u - Y(x_u)$	$(Y_u - Y)^2$	$\{Y(x_u) - Y\}^2$	$\{Y_u - Y(x_u)\}^2$
1	50	49.48	0.52	115.98	127.45	0.27
2*	63	62.40	0.60	4.98	2.66	0.36
3	56	55.95	0.05	22.75	23.22	0.00
4*	62	62.40	-0.40	1.51	2.66	0.16
5*	62	62.40	-0.40	1.51	2.66	0.16
6	63	63.59	-0.59	4.98	7.96	0.35
7	50	50.79	-0.79	115.98	99.59	0.62
8*	62	62.40	-0.40	1.51	2.66	0.16
9	67	67.52	-0.52	38.82	45.57	0.27
10	68	67.21	0.79	52.28	41.48	0.62
11	59	58.41	0.59	3.13	5.57	0.35
12	65	65.05	-0.05	17.90	18.32	0.00
13*	63	62.40	0.60	4.98	2.66	0.36
$\Sigma Y_u = 790$				TSS = 386.31	SSR = 382.46	SSE = 3.68

* indicates replicate points at the centre

1. Calculation of mean response

$$Y = \Sigma Y_u / \Sigma N = 790 / 13 = 60.77$$

2. Calculation of Sum of Squares for Model

$$\begin{aligned} SSR &= \Sigma \{Y(x_u) - Y\}^2 = (-11.29)^2 + (1.63)^2 + \dots + (1.63)^2 \\ &= 382.46 \end{aligned}$$

$$\text{degrees of freedom} = p = 6$$

3. Calculation of Total Sum of Squares

$$\begin{aligned} TSS &= \Sigma (Y_u - Y)^2 = (-10.77)^2 + (2.23)^2 + \dots + (2.23)^2 \\ &= 386.31 \end{aligned}$$

$$\text{degrees of freedom} = n = 13$$

4. Calculation of Residual Sum of Squares

$$SSE = \{Y_u - Y(x_u)\}^2 = (0.52)^2 + (0.062)^2 + \dots + (0.062)^2 = 3.68$$

$$\text{degrees of freedom} = n - p = 13 - 6 = 7$$

5. Calculation of Sum of Squares due to Pure Error (5 replicates)

$$Y_{u.} = \Sigma Y_{ui} / g = (Y_2 + Y_4 + Y_5 + Y_8 + Y_{13}) / 5 = 62.4$$

$$SS_{PE} = \Sigma (Y_{ui} - Y_{u.})^2 = (0.6)^2 + (-0.4)^2 + \dots + (0.6)^2 = 1.20$$

$$\text{degrees of freedom} = g - 1 = 5 - 1 = 4$$

6. Calculation of Sum of Squares due to Lack of fit

$$SS_{LOF} = SSE - SS_{PE} = 3.68 - 1.20 = 2.48$$

$$\text{degrees of freedom} = (n - p) - (g - 1) = 7 - 4 = 3$$

7. F-Test

$$F_{\text{calculated (model)}} = MSRG / MSRS = 120.26$$

$$F_{0.05 (6,7)} = 3.87 \text{ (from standard tables)} < F_{\text{calculated (model)}}$$

Test is Significant

$$F_{\text{calculated (Lack-of-fit)}} = MSL / MSE = 2.77$$

$$F_{0.05 (3,4)} = 6.59 \text{ (from standard tables)} > F_{\text{calculated (Lack-of-fit)}}$$

Lack of fit is insignificant

Therefore the model is adequate.

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